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KIADJA:
A SZEGEDI TUDOMÁNYEGYETEM
Felelős szerkesztő: Dr. Kiss Árpád

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Direktor: Prof. Dr. Á. Kiss.

Zur Lösungsmittelabhängigkeit der Extinktionskurven von polycyklischen Komplexen.

Von Á. Kiss und S. Szőke.

(Eingegangen im Januar 1948).

1. *Einleitung.*

Der Einfluss des Lösungsmittels wurde bereits in den früheren Arbeiten (1) gestreift. Die Beantwortung dieser verwickelten Frage ist die Aufgabe der jetzigen Arbeit.

Die Experimentelle Einrichtung und die Messmethode betreffend verweisen wir auf frühere Arbeiten (2). Die Komplexe: 2-Oxybenzalanilin-Nickel (I), Salicylaldehyd-aethylendiimin-Nickel (II), 2-Aminobenzaldehyd-2'-phenylendiimin-Nickel (III), 2-Oxybenzalanilin-Kupfer (IV), 2-Oxybenzal-4'-oxyanilin-Kupfer (V), 8-Oxychinolin-Kupfer (VI), wurden wie früher (1) beschrieben hergestellt. Die Lösungsmittel wurden nach Weigert (3) gereinigt. Die Reinheit der Komplexe, bzw. die Konzentration der Lösungen wurden analytisch kontrolliert.

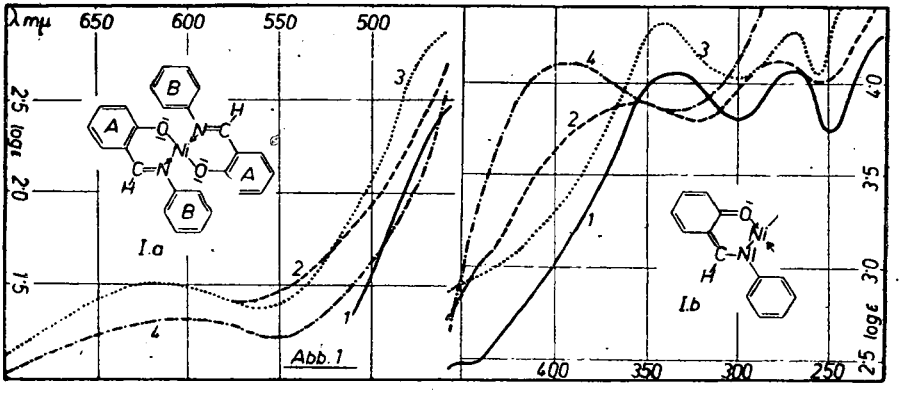

Abb. 1. 2-Oxybenzalanilin-Nickel (I). Kurve 1: Aethanol. K. 2: Propanol. K. 3: Chloroform. K. 4: Pyridin.

2. *Komponenten des Lösungsmitteleinflusses.*

Durch die Lösungsmittel werden die Extinktionskurven der Komplexe verwickelter Weise geändert. Es sind zwei idealisierte Wirkungsarten zu unterscheiden.

A) Die zwischen dem Komplex und den Molekülen des polaren Lösungsmittels wirkenden Kräfte beeinflussen das ganze Molekül des Komplexes. Als eine Folge dieser, von mehreren Lösungsmittelmolekülen ausgeübten Wirkungen ist z. B. die Solvatation des gelösten Moleküls, welche zu keiner Absättigung nach stöchiometrischen Gesetzen führt.

B) Die an den unbesetzten Koordinationsstellen, bzw. an den reaktionsfähigen Atomen des Komplexes angelagerten Lösungsmittelmoleküle führen, wegen der Lokalisierung der Wirkungskräfte, zur Bildung von Verbindungen nach stöchiometrischen Gesetzen.

Beide Wirkungen treten oft gemeinsam auf. So ist die isolierte Feststellung beider Effekte schwer durchzuführen. Ausserdem kann das Lösungsmittel den Assoziationsgrad der Komplexe ändern (4). Da bei den untersuchten Komplexen gefunden wurde, dass ihre Extinktionskurven beinahe konzentrationsunabhängig sind, so kann die Assoziation kaum eine grössere Rolle spielen und kann deshalb ausser Betracht gelassen werden.

Die untersuchten Komplexe sind mit planer Anordnung der Liganden (6) nach der Koordinationszahl vier aufgebaut. Somit überwiegt die unter *B* erwähnte Wirkung. Die polaren Lösungsmittelmoleküle werden durch eine semipolare Bindung festgehalten.

Im Falle einer planen Anordnung der Liganden (6) wird mindestens der Ring *B* (Vgl, Ia, Ic, und Va Abb. 1, 2 und 8) aus

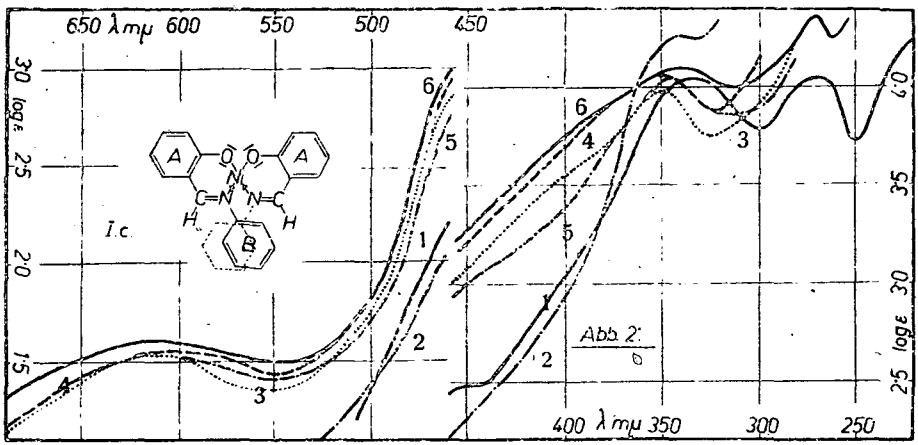

Abb. 2. 2-Oxybenzalanilin-Nickel. (1). Kurve 1: Aethanol. K. 2: Aceton. K. 3: Benzol. K. 4: Toluol. K. 5: Xylol. K. 6: Kohlenstofftetrachlorid.

der Ebene des Komplexes hinausgedrängt. Die sterische Hinderung ist bei der Form Ic (Abb. 2) grösser, als bei der Form Ia (Abb. 1) Gleich sind die Verhältnisse bei V, es wurde deshalb die Form Vc bei diesem Komplex nicht angegeben (Vgl. Ic, Abb. 2). Wegen der starken sterischen Hinderung kann anstatt der streng planen Anordnung der Liganden ein Übergangstyp der planen und Tetraeder-Konfiguration sich ausbilden (Vgl. 7). Da dieser Umstand den Lösungsmitteleinfluss wesentlich nicht beeinflusst, beabsichtigen wir dieser Frage erst nach Beendigung der dipolmoment Messungen, nachzugehen.

3. *Zum Mechanismus der Lichtabsorption.*

Die Kurven der untersuchten Komplexe bauen sich verwickelter Weise aus der Eigenabsorption des Zentralions der koordinativen Bindungselektronen und der Liganden auf (1)

Wenn auch in den Koplexen je ein einsames Elektronenpaar der Stickstoff- und Sauerstoffatome durch die Komplexbildung fest-

gehalten wurde, kann doch eine Resonanz der Grenzstrukturen der Liganden bestehen (1). Bei den benzoidalen (Ia Abb. 1), bzw. chinoidalen (Ic Abb. 1) Grenzformen bindet das Sauerstoff-, bzw. das Stickstoffatom mit den Hauptvalenzen. Dies bestätigt der experimentelle Befund (1), dass die selektive Absorption der Liganden in ihren polycyklichen innerkomplexen Verbindungen beibehalten bleibt. Dies zeigt uns ein Vergleich der Kurven der Ausgansstoffe und dieser ihrer Komplexe (1).

Die Wirkung *A* kann die Übergangswahrscheinlichkeit, die Anregungsenergie und die relative Häufigkeit der Grenzstrukturen des Grund- und Anregungszustandes beeinflussen (1 vgl. auch 4). Somit ruft sie keine neue Anregungsvorgänge hervor (1). Wirkung *B* kann, besonders im Falle von semipolar gebundenen Lösungsmittelmolekülen mit neuen Anregungsvorgängen die Kurve des Komplexes ändern.

Die Strukturänderung der Kurven können bedingt sein durch die Lagen- und Höhenänderung einer konsatänten Anzahl von Banden (Wirkung *A*), bzw. durch Auftreten von neuen Banden

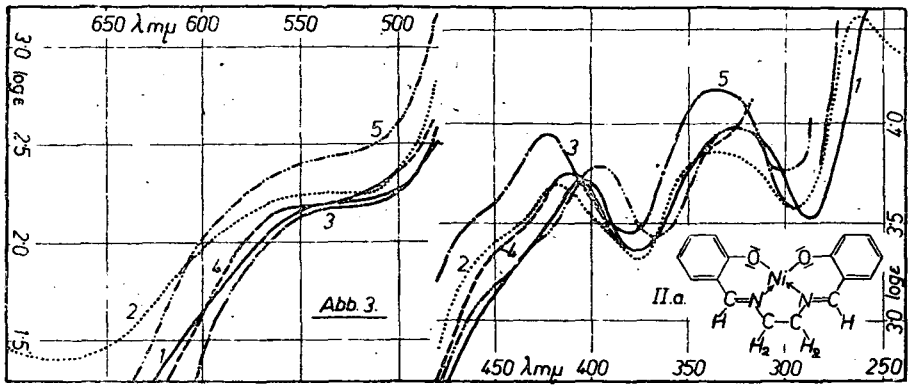

Abb. 3. Salicylaldehyd-aethylendiimin-Nickel. (II). Kurve 1: Aethanol. K. 2: Chloroform. K. 3: Benzol. K. 4: Aceton. K. 5: Pyridin.

(Wirkung *B*). Somit ist es in einem gegebenen Falle schwer zu entscheiden, welche der beiden Wirkungen die Strukturänderung der Kurven verursacht. Dazu kommt noch, dass bei grösseren organischen Molekülen, wie es z.B. die Liganden der untersuchten Komplexe sind, die einzelnen Teile des Moleküls demselben Lösungsmittel gegenüber sich verschieden verhalten. Weiterhin sind die Wirkungen der Lösungsmittel bei den einzelnen Komplexen ganz spezifisch (1). Somit kann man einstweilen kaum voraussagen, welche der beiden Wirkungsarten die Kurven des betreffenden Komplexes beeinflussen wird. Es kann weder die Richtung, noch die Grösse beider Wirkungen nach keiner Theorie abgeschätzt werden. So ist man einstweilen an das Sammeln von zuverlässigen Versuchsdaten angewiesen.

4. *Die Besprechung der Versuchsdaten.*

Bei der Untersuchung des Lösungsmitteleinflusses (im Sinne des im Kap. 2 und 3 Gesagten) sollten die in Normalbenzin gemessenen Extinktionskurven als Bezugsspektren gewählt werden. Da

jedoch die untersuchten Komplexe in Hexan durchaus unlöslich sind, mussten die in Aethanol erhaltenen Kurven als Bezugsspektren gewählt werden, was wegen des spezifischen Lösungsmitteleinflusses die Aufklärung der gestellten Fragen erschwert. Dieser Umstand, dass die Verbindungen nur in polaren Lösungsmitteln gut löslich sind, zeigt, dass beim Lösen die Solvatation, bzw. die Wirkung *B* eine grosse Rolle spielt.

Zur ersten Orientierung wurden die Kurven von möglichst verschieden zusammengesetzten polycyklischen innerkomplexen Ver-

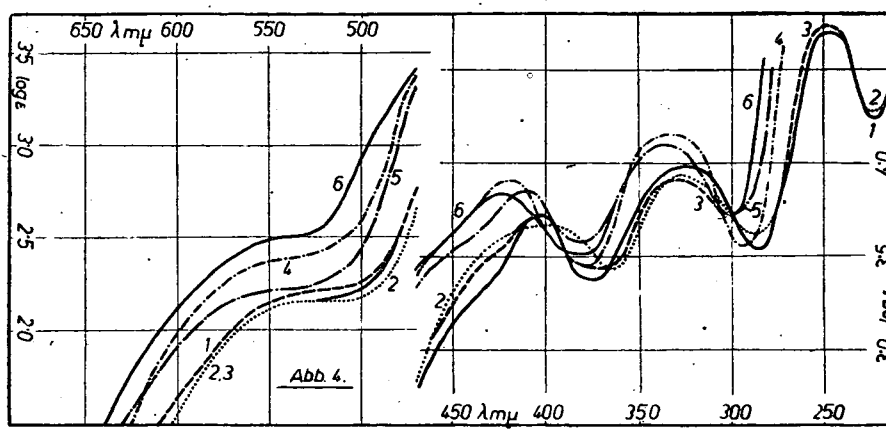

Abb. 4. Salicylaldehyd-aethylendiimin-Nickel (II). Kurve 1: Aethanol. K. 2: Methanol. K. 3: Benzol. K. 4: Aceton. K. 5: Pyridin.

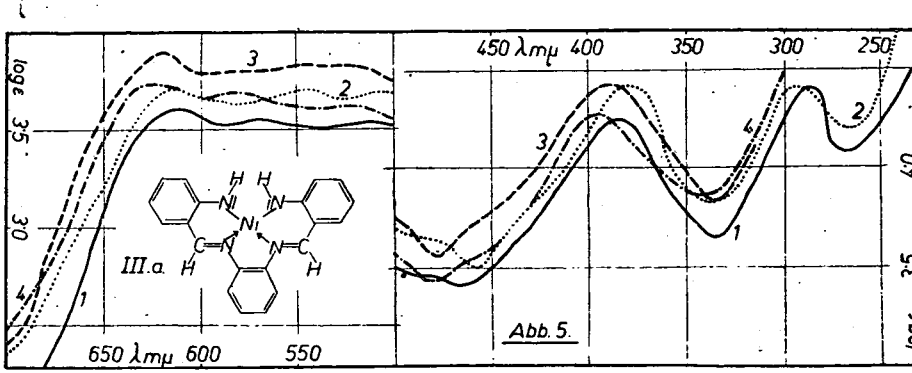

Abb. 5. 2-Aminobenzaldehyd-o-phenylendiamin-Nickel. (III). Kurve 1: Aethanol. K. 2: Chloroform. K. 3: Benzol. K. 4: Pyridin.

bindungen des Kupfers und Nickels ausgemessen. Die systematische Untersuchung von Detailfragen wird für späteren Beiträgen vorbehalten.

Der Kürze wegen sehen wir von der Besprechung der in Abb. 1 bis 10 widergegebenen einzelnen Kurven ab. Wie ihr Verlauf zeigt, ist der Lösungsmitteleinfluss im Sichtbaren und an der Grenze desselben stärker, als im Ultraviolett. Dies zeigt, dass die Eigenabsorption des Kupfer- und Nickelions und diese der koordinativen Bindungselektronen stärker geändert wird, als diese der aromati-

schen Liganden. Dies steht mit der Bindungsstärke, bzw. mit der Anregungsenergie der Erwehnten Elektronen in Zusammenhang (1). Diese Frage kann aber an Mangel von entsprechenden Elektronenverteilungs-Modellen der Komplexe einstweilen nicht näher nachgegangen werden. Auch in dieser Richtung sind weitere Untersuchungen im Gange.

Die Lösungsmittel wirken bei den einzelnen Komplexen ganz spezifisch (Abb. 1—10). Die Ursache dessen ist, dass die Wechselwirkungskräfte so von den Lösungsmitteln, als auch von den gelösten Komplexen abhängen. Der Lösungsmitteleinfluss ist bei den Nickelkomplexen allgemein grösser, als bei den Kupferverbindungen (Abb.

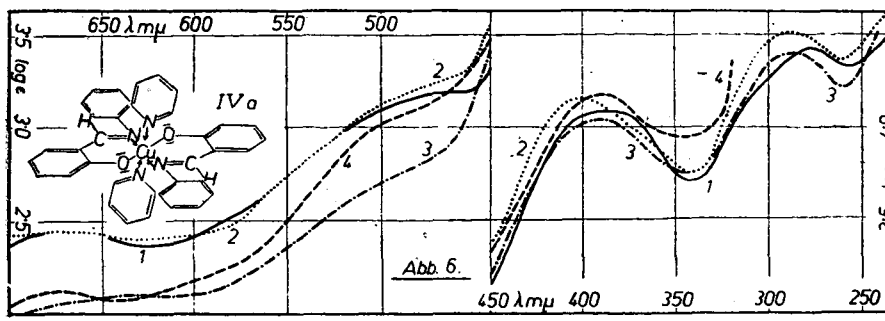

Abb. 6. 2-Oxybenzalanilin-Nickel IV). Kurve 1: Aethanol. K. 2: Chloroform. K. 3: Kohlenstofftetrachlorid. K. 4: Aceton.

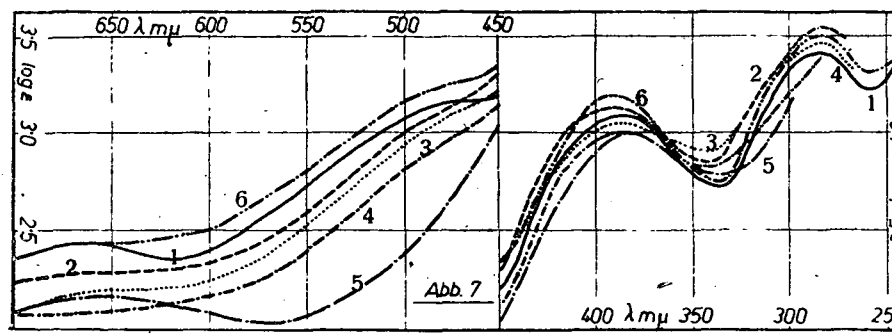

Abb. 7. 2-Oxybenzalanilin-Kupfer (V). Kurve 1: Aethanol. K. 2: Benzol. K. 3: Toluol. K. 4: Xylol. K. 5: Pyridin. K. 6: Propanol.

1 u. 2, bzw. 6 u. 7). Da die letztgenannten allgemein stabiler sind, so spielt auch die Stabilität der Komplexe eine Rolle. So verursachen bei I (Abb. 1 u. 2) die polaren Lösungsmittel eine stärkere Extinktionszunahme und Verschiebung der Banden nach den langen Wellen, als bei IV (Abb. 6 u. 7). Bezogen auf die aethanolische Kurve wird die Extinktion durch Benzol bei I erhöht (Abb. 2), bei IV (Abb. 7) verringert.

Wie früher gezeigt wurde (1) ist der Lösungsmitteleinfluss bei den, nach der Koordinationszahl 3 aufgebauten Komplexen des 2-Oxybenzal-2'-oxyanilins besonders stark. Hier dringt das Lösungsmittelmolekül in die unbesetzte vierte Koordinationsstelle ein.

Darauf weist der grosse Unterschied der in Pyridin und in ammoniakalischer Lösung gemessenen Kurven bezogen auf die aethanolische Kurve hin (1). Diese Frage wird in einem späteren Beitrag ausführlicher behandelt.

Die Verwischung der Struktur der in Pyridin gemessenen Kurven (Abb. 3, 5, 7, 8 u. 9) weist auf die starke Wechselwirkung zwischen Pyridin und Komplex hin. Es entstehen wahrscheinlich komplexe mit zwei Pyridinmolekülen in trans Stellung (Vgl. IVa Abb. 6).

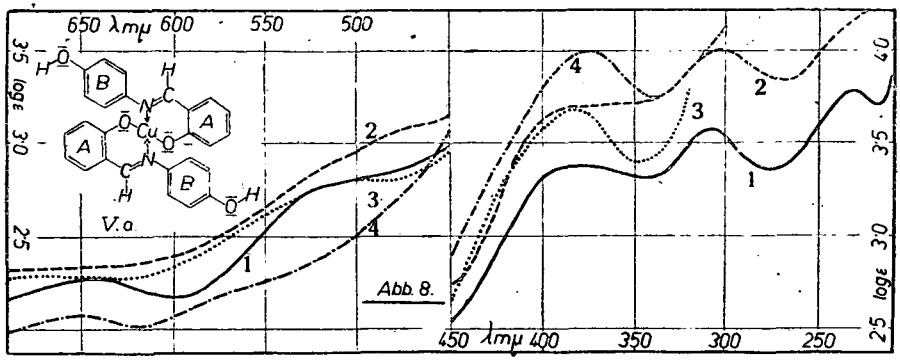

Abb 8. 2-Oxybenzal-4'-oxyanilin-Kupfer (V). Kurve 1: Aethanol. K. 2: Chloroform. K. 3: Aceton. K. 4: Pyridin.

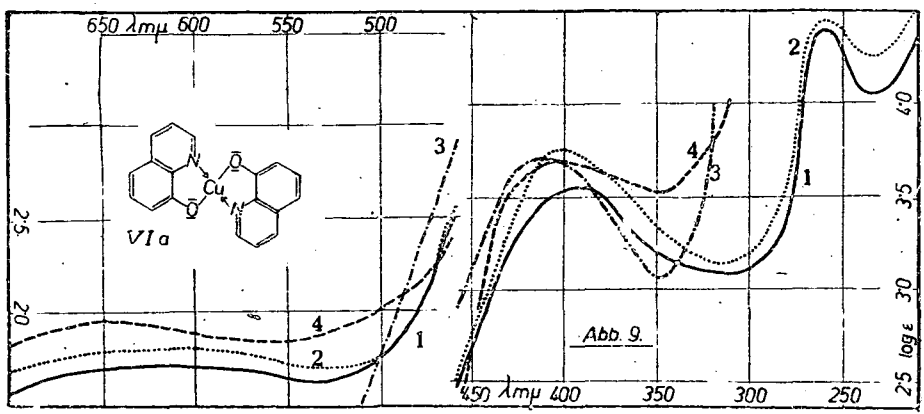

Abb. 9. 8-Oxychinolin-Kupfer (VI). Kurve 1: Aethanol. K. 2: Propanol. K. 3: Aceton. K. 4: Pyridin.

Von der Wirkung der einzelnen Lösungsmittel kann zusammengefasst noch folgendes gesagt werden.

In Propanol nimmt die Extinktion in langwelligem Spektralgebiet allgemein zu (Abb. 1, 4, 7 u. 9), und zwar in grösserem Masse bei Nickel- (Abb. 1 u. 4), als bei Kupfer-Komplexen (Abb. 7 u. 9). Die Eigenabsorption der Liganden wird kaum geändert.

In Benzol, Xylol und Toluol nimmt die Extinktion in der angeschreibenen Reihe (Abb. 2, 4, 5 u. 10), mit Ausnahme des Komplexes IV (Abb. 6 u. 7) zu, und die Kurve wird nach den

langen Wellen verschoben. Gleicher Weise wirken Kohlenstoffterachlorid und Aceton (Abb. 2, 3, 8, 9 u. 10). Bei IV (Abb. 6 u. 7) wird die Extinktion durch Benzol, Xylol, Kohlenstofftetrachlorid und Aceton geschwächt (Abb. 6 u. 7). Chloroform wirkt bei den untersuchten Komplexen ganz spezifisch (Abb. 1, 3, 5, 6 u. 8).

Nach Scheibe (8) besteht eine einfache Gesetzmässigkeit zwischen dem Dipolmoment des Lösungsmittels und der Extinktion des homeopolaren, gelösten Stoffes. Dies besteht nicht bei den untersuchten Komplexen, was im Sinne des im Kap. 2 und 3 Gesagten vorauszusehen ist.

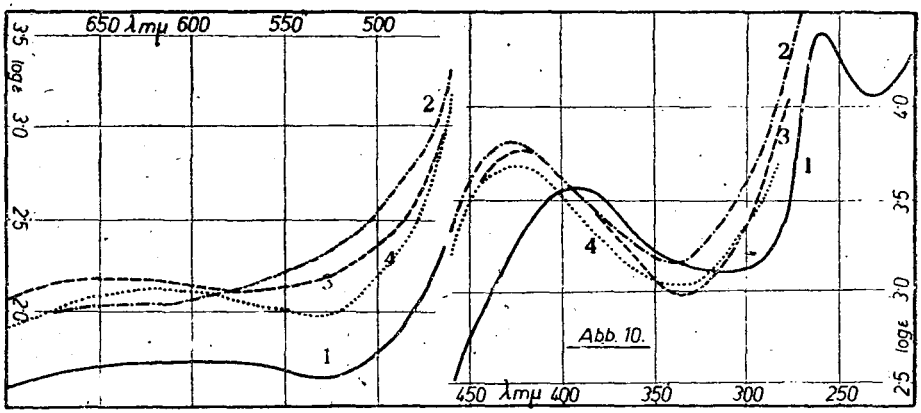

Abb. 10. 8-Oxychinolin-Kupfer (VI). 1: Aethanol. K. 2: Benzol. K. 3: Xylol. K. 4: Kohlenstofftetrachlorid.

Zusammenfassung.

Es wurden die Extinktionskurven von sechs polycyklischen innerkomplexen Verbindungen in Methanol, Aethanol, Propanol, Aceton, Chloroform, Kohlenstofftetrachlorid, Benzol, Toluol, Xylol und Pyridin zwischen 200 und 700 mμ ausgemessen.

Durch die erwähnte Lösungsmittel werden die Eigenabsorptionen des Zentralions und der koordinativen Bindungselektronen stärker geändert, als diese der aromatischen Liganden.

Der ganz spezifische Einfluss der Lösungsmittel dürfte bedingt sein: durch auf das ganze Molekül des Komplexes ausgeübte Wirkung *A*, bzw. durch eine Anlagerung der Lösungsmittelmoleküle in trans Stellung an die zwei freien Koordinationsstellen des Komlexes, oder an die reaktionsfähigen Atome der Liganden (Wirkung *B*). Durch beide Effekte wird die Anregungsenergie und die Übergangswahrscheinlichkeit verwickelter Weise geändert.

Weitere Untersuchungen sind im Gange.

Szeged (Ungarn) Januar 1948.

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On the absolute entropy of diatomic and polyatomic gases

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The quantum statistics of the monatomic gases were treated by Planck[1] in two papers. In his first paper he considered continuous phase points in the phase space, in the second paper he only assumed definite phase points.

In my paper *I* generalise Planck's fundamental assumptions. *I* calculate with simple statistical methods the absolute entropy of the diatomic and polyatomic gases. My assumptions are as follows: The diatomic and polyatomic gas are ideal gases. The molecules are considered to be rigid, the motions of the atoms and electrons are not taken into consideration. By the counting of the phase probability it is not necessary to treat independently the phase probability referring to the rotational coordinates.

1. Let us consider a gramme molecule of a diatomic gas consisting of N molecules, having volume V and temperature T. To calculate the probability of the given state we divide the 10 N dimensional phase space of the gas — a molecule has 3 translational and 2 rotational coordinates and 5 corresponding momenta — into cells. The cells may be equal or different in volume. To maintain the generality *I* investigate cells of different size: $P_1 h^{5N}$, $P_2 h^{5N} \ldots$, in which h is Planck's constant, P_1, $P_2 \ldots$ denote the statistical weight of cells. The thermodynamical behaviour of the gas is determined by the following equation of free energy

$$F = -kT \log \left(\sum P_n e^{-\frac{u_n}{kT}} \right) \qquad (1)$$

in which U_n denotes the energy of the n *th* elemental region. Expressing the energy U_n with the energies of the single molecules we obtain

$$F = -kT \log \sum p_n e^{-\frac{u}{kT}} \tag{2}$$

where u, gives the energy of the n *th* elementar region in the phase space of a molecule. To determine u, we must consider that in (2) the term number of $\sum_{\text{for states}}$ agrees with the number of the cells in the phase space of a molecule. The total number of the cells in (2) is

$$z = \frac{1}{h^{5N}} \iiint \ldots dx_1 dy_1 dz_1 \ldots d\vartheta_1 d\varphi_1 \ldots dp_{x1} dp_{y1} dp_{z1} \ldots dp_{\vartheta 1} dp_{\varphi 1} \ldots \tag{3}$$

in which $x_1, y_1, z_1 \ldots$ denote the translational coordinates of the molecule $1 \ldots, \vartheta_1, \varphi_1 \ldots$ are the polar coordinates for the determination of the positive direction of the symmetrical axis of the molecule $1 \ldots, p_{x1}, p_{y1}, p_{z1}$ denote the corresponding impulse coordinates, by each molecule the integration has to be extended over all possible values of the coordinates between energy 0 and u. We must divide in equation (3) by $N!$, for with any state fixed by a system of coordinates, there are $N!$ different state points to be considered. Integrating in equation (3) and denoting the moment of inertia with I it is[2]

$$z = \frac{1}{N!\, h^{5N}} \cdot \frac{V^N (4\pi)^N \pi^{\frac{5N}{2}} I^N (\sqrt{m^3})^N (\sqrt{2u})^{5N}}{\Gamma\left(\frac{5}{2}+1\right)^N}. \tag{3a}$$

Using the Stirling approximation for factorial $N!$ and writing $\Gamma\left(\frac{5}{2}+1\right) = \frac{15\sqrt{\pi}}{8}$, it becomes

$$z = \left(\frac{32\pi^3 e I \sqrt{m^3} \sqrt{(2u)^5} V}{15 h^5 N} \right)^N. \tag{3b}$$

2. In the phase space of a molecule the sum of the statistical weights p_1, p_2, $p_3 \ldots$ is equal to the number of the cells of size h^5, i. e.

$$(p_1 + p_2 + \ldots + p_n)^N = \left(\frac{32\pi^3 e I \sqrt{m^3} \sqrt{(2u)^5} V}{15 h^5 N} \right)^N. \tag{4}$$

For determining the interdependence between the sum of the statistical weights and the number of the cells of different size we can only put forward suggestions. In the following I generalise Planck's assumption referring to the monatomic gases, according to which in the phase space of a molecule the sum of the statistical weights belonging to the cells of different size is equal to the number of cells raised to power of the coordinate number, i. e.

$$p_1 + p_2 + \ldots + p_n = n^5. \tag{5}$$

From equations (4) and (5) we find

$$n^5 = \frac{32\pi^3 e I \sqrt{m^3} \sqrt{(2u)^5} V}{15 h^5 N} \tag{6}$$

and

$$u = \frac{1}{2} \left(\frac{15 h^5 N}{32\pi^3 e I \sqrt{m^3} V} \right)^{2/5} n^2. \tag{7}$$

The quantum energy of the n *th* cells is generalising Panck's procedure

$$u_n = \frac{1}{2}\left(\frac{15h^5N}{32\pi^3 el\sqrt{m^3V}}\right)^{2/5}(n-\alpha)^2, \tag{8}$$

in which α is a constant, positive, proper fraction. If $\alpha = 0$ the quantum energy gives the extreme energy of cells. The free energy in (2)

$$F = -RT\log\sum_{n=1}^{\infty}[(n+1)^5 - n^5]\,e^{-\sigma(n-\alpha)^2}, \tag{9}$$

where $$\sigma = \frac{1}{2kT}\left(\frac{15h^5N}{32\pi^3 el\sqrt{m^3V}}\right)^{2/5}.$$

At high temperatures ($\sigma << 1$)

$$F = -RT\log\int_1^{\infty} e^{-\sigma(n-\alpha)^2}dn^5,$$

$$F = -RT\log\left\{5\int_0^{\infty}(x+n_0)^4 e^{-\sigma x^2}dx - 5\int_0^{1-\alpha}(x+n_0)^4 e^{-\sigma x^2}dx\right\}. \tag{11}$$

The second integral can be neglected and[3]

$$F = -RT\log\left\{\frac{5.4!\sqrt{\pi}}{\sigma^{5/2}2^6} + \frac{10\alpha}{\sigma^2} + \frac{10\alpha^2\sqrt{\pi}}{2\sigma^{3/2}} + \frac{10\alpha^3}{\sigma} + \frac{5\alpha^4\sqrt{\pi}}{2\sigma^{1/2}}\right\}. \tag{12}$$

Raising out of the first term in logarithm the log. of the second part ($\sigma << 1$) can be neglected. Therefore

$$F = -RT\log\frac{8\pi^2 el\sqrt{(kT)^5}\sqrt{(2m\pi)^3}V}{h^5N}. \tag{13}$$

Hence

$$S = R\log\frac{8\pi^2 e^{7/2} I\sqrt{(kT)^5}\sqrt{(2m\pi)^3}V}{h^5N}. \tag{14}$$

This equation agrees with the equation determined by Tetrode[4], and if we do not take the symmetrical number into consideration, with the value calculated by Ehrenfest[5] and Trkal. Ehrenfest and Trkal have determined the chemical constant of gases. From this the entropy must be calculated.

3. Let us now investigate a gramme molecule of a polyatomic gas consisting of N molecules, having tempserature T, inclosed within the volume V. The total number of cells in (2) is

$$z = \frac{1}{h^{6N}N!}\iint\ldots dx_1 dy_1 dz_1 \ldots d\vartheta_1 d\varphi_1 d\psi_1 \ldots dp_{x_1} dp_{y_1} dp_{z_1} \ldots$$
$$\ldots dp_{\vartheta_1} dp_{\varphi_1} dp_{\psi_1} \ldots, \tag{15}$$

in which x_1, y_1, z_1 are the translational coordinates of the molecule $1\ldots$, ϑ_1, φ_1 respectively $\psi_1\ldots$. denote the angles of the positive direction of the third *(L)*, respectively first *(I)* principal moment of inertia of the molecule $1\ldots$, p_{x1}, p_{y1}, p_{z1}. $p_{\vartheta 1}$, $p_{\varphi 1}$, $p_{\psi 1}$..... are the corresponding impulse coordinates, the integration by each molecule has to be extended over all possible values of the coordinates bet-

ween energy 0 and u. Denoting the principal moments of inertia of a molecule with I_1, K, L the energy[6] of a molecule becomes

$$u = \frac{1}{2m}(p_x^2+p_y^2+p_z^2)+\frac{1}{2}\{I(\sin\vartheta\cos\psi\dot{\varphi}-\sin\psi\dot{\vartheta})^2+$$
$$+K(-\sin\vartheta\sin\psi\dot{\varphi}-\cos\psi\dot{\vartheta})^2+L(\cos\vartheta\dot{\varphi}+\dot{\psi})^2\},$$
$$u = \frac{1}{2m}(p_x^2+p_y^2+p_z^2)+\frac{1}{2}(Ia^2+Kb^2+Lc^2), \qquad (16)$$

in which a, b, c are the components of the rotational velocity relating to the principal axes of inertia and

$$a=\sin\vartheta\cos\psi\dot{\varphi}-\sin\psi\dot{\vartheta},\quad b=-\sin\vartheta\sin\psi\dot{\varphi}-\cos\psi\dot{\vartheta},$$
$$c=\cos\vartheta\dot{\varphi}+\dot{\psi}. \qquad (17)$$

The interdependence among the impulse coordinates and a, b, c from equations (16), (17) is

$$\left.\begin{aligned} p_\vartheta &= -Ia\sin\psi - Kb\cos\psi \\ p_\varphi &= Ia\sin\vartheta\cos\psi - Kb\sin\vartheta\sin\psi + Lc\cos\vartheta \\ p_\psi &= Lc. \end{aligned}\right\} \qquad (18)$$

Introducing in equation (15) a_1, b_1, $c_1\ldots$ instead of $p_{\vartheta_1}, p_{\varphi_1}, p_{\psi_1}, \ldots$ we find

$$z=\frac{1}{h^{6N}N!}\iint\ldots dx_1\,dy_1\,dz_1\ldots d\vartheta_1\,d\varphi_1\,d\psi_1\ldots dp_{x_1}\,dp_{y_1}\,dp_{z_1}\ldots$$
$$\ldots IKL\sin\vartheta_1\,da_1\,db_1\,dc_1\ldots, \qquad (19)$$

integrating

$$z=\left(\frac{4\pi^5 e\sqrt{IKLm^3}\sqrt{(2u)^6}V}{3h^6N}\right)^N. \qquad (20)$$

The sum of the statistical weights belonging to the cells of different size in the phase space is in agreement with the assumption given by diatomic gases

$$p_1+p_2+\ldots+p_n=n^6, \qquad (21)$$

in which n is the number of the cells of different size. From equations (20) and (21)

$$n^6=\frac{4\pi^5 e\sqrt{IKLm^3}\sqrt{(2u)^6}V}{3h^6N} \qquad (22)$$

and

$$u=\frac{1}{2}\left(\frac{3h^6N}{4\pi^5 e\sqrt{IKLm^3}V}\right)^{1/3}n^2.$$

The quantum energy of the n *th* cells is given by

$$u_n=\frac{1}{2}\left(\frac{3h^6N}{4\pi^5 e\sqrt{IKLm^3}V}\right)^{1/3}(n-a)^2. \qquad (23)$$

The free energy therefore is substituting

$$\sigma=\frac{1}{2kT}\left(\frac{3h^6N}{4\pi^5 e\sqrt{IKLm^3}V}\right)^{1/3}$$

$$F=-RT\log\sum_{n=1}^{\infty}[(n+1)^6-n^6]\,e^{-\sigma(n-\alpha)^2}. \qquad (24)$$

At high temperatures ($\sigma << 1$)

$$F = -RT \log \int_0^\infty e^{-\sigma(n-\alpha)^3} dn^6, \tag{25}$$

$$F = -RT \log \left\{ 6 \int_0^\infty (x+\alpha)^5 e^{-\alpha x^3} dx - 6 \int_0^{1-\alpha} (x+\alpha)^5 e^{-\alpha x^3} dx \right\}. \tag{26}$$

Following the procedure according to equation (11) it becomes

$$S = R \log \frac{8\pi^2 e^{5/2} \sqrt{IKLm^3} \sqrt{(2\pi kT)^6}\, V}{h^6 N}, \tag{27}$$

which is identical with the equation given by Tetrode[7], and without considering the symmetrical number, with the value calculated by Ehrenfest[8] and Trkal.

Summary

The absolute entropy of diatomic and polyatomic gases have been calculated with simple statistical methods on the base of Planck's fundamental assumptions. The obtained results are in agreement with the values determined by Tetrode, Ehrenfest and Trkal.

References

1. *M. Planck:* Sitzungsber. d. Berl. Akademie d. Wiss. p. 653. 1916 and p. 49. 1925.

2. The volume of an f dimensional sphere of radius r is

$$V = \frac{\sqrt{\pi^f}\, r^f}{\Gamma\left(\frac{f}{2}+1\right)}$$

T. H. Schoute: Mehrdimensionale Geometrie, Sammlung Schubert 1905. II. p. 289.

From this the volume of the ellipsoid having different axes can be calculated. In (3) the integration has to be extended by each molecule between energy o and

$$u = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \frac{1}{2I}(p_\vartheta^2 + \overline{p}_\varphi^2) \quad \left(\text{substituting} \quad \overline{p}_\varphi = \frac{p_\varphi}{\sin\vartheta}\right).$$

3 $$\int_0^\infty e^{-tx^2} x^{2n+1} dx = \frac{n!}{2t^{n+1}}, \int_0^\infty x^{2k} e^{-tx^2} dx = \frac{1}{t^k \sqrt{t}} \frac{(2k)! \sqrt{\pi}}{2^{2k+1} k!}.$$

4. *H. Tetrode:* Proceedings of the Section of Sciences (Amsterdam), 17. p. 1175, equation (17), 1915.

5. *P. Ehrenfest and V. Trkal:* Ann. Thys. 65. p. 624. 1921.

6. *M. Planck:* Einführung in die allgemeine Mechanik, 1928, § 146, 147 and 152.

7. *H. Tetrode:* Proceedings of the Section of Sciences (Amsterdam), 17. p. 1181. equation (34), 1915.

8. *P. Ehrenfest and V. Trkal:* Ann. d. Thys. 65. p. 624, 1921.

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Synthesis of some new hydrazine derivatives of thiazol.

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In the search for new, more active chemotherapeuticals (1) it deemed of interest to synthesize 2-hydrazino-thiazols and some of their sulfanilyl derivatives, especially as other hydrazine derivatives of sulfanilic acid (2, 3) were found to be effective against different bacteria; e. g. Sulfanilyl thiosemicarbazide proved to be efficient against different Clostridia strains (3). We suggested that ring closure of this molecule to the corresponding 2(2′-sulfanilyl-hydrazino)-4-methyl-thiazol II bring about an increase of antibacterial activity all the more as sulfamethylthiazol proved more active than sulfanilyl thiocarbamide. On the other hand, it seemed worthy to synthesize the 1′-sulfanilyl-isomer of II (IV) in order to compare its antibacterial activity with that of the 2′-sulfanilyl analogue II.

For this reason we attempted to prepare first 2-hydrazino-4-methyl-thiazol. 2-Hydrazino thiazol and its homologues were as yet not described, with the exception of the preparation of its 2′-aryl derivatives (4) and of 2.2′-hydrazino-bis-thiazol (5). Diazonium salts (6) resp. nitrimines (7) from amino thiazols could not yet be isolated (8). In solution these salts copulate normally with phenols, etc. (9), but they tend to give diazoamido compounds (10). Considering their sensibility, their reduction to the corresponding hydrazines was not yet carried out. We reduced the diazonium chloride from 2-amino-4-methyl-thiazol using methods which are suitable for the preparation of primary hydrazines, but we failed to obtain appreciable amounts of the excepted 2-hydrazino-4-methyl-thiazol. Sodium sulfite reduction led to the isolation of the sodium salt of the corresponding hydrazine N-sulfonic acid, however, we did not succeed in removing the sulfonic group without destroying the molecule. On the other hand, our reduction experiments with stannous chloride furnished as a single basic product 2-amino-4-methyl-thiazol, identified through its picrate (11) and acetylsulfanilyl derivative (12). Its formation can be explained, assuming acid hydrolysis of the nitrosimino derivative (tautomeric form of the diazonium hydroxyde) during the reduction. We interrupted these reduction experiments and wanted to build up 2(1′-sulfanilyl-hydrazino)-4-methyl-thiazol in an indirect way.

One plan was to synthesize 2(2′.2′dibenzylhydrazino)-4-methyl-thiazol (Va) in which only the nitrogen atom in 1′position would be able to react with an acyl chloride to secure a sulfanilyl-hydrazine Vb, closely related chemically and perhaps pharmacologically too, to sulfamethyl-thiazol. It was anticipated that benzyl groups would be removed by hydrogenolyiss to furnish IV.

Va was synthesized by converting as-dibenzyl-hydrazine (13) (VI) by means of hydrogene thiocyanate, resp. with thiocarbamide

into the oily 1.1-dibenzyl-thiosemicarbazide (VII); this was condensed in turn with monochloro acetone to Va. Another method consisted of a condensation of VI with thiocyano acetone (14) to Va. Acylation of the latter gave an acetyl derivative Vc, however, with benzene sulfonyl chloride it failed. This was attributed to steric hindrance, caused by the two benzyl groups and by the thiazol nucleus. A prototropic change (15) of Va into a thiazolon-hydrazone, like Vd, would not cause the failure of the reaction (16).

In the presence of palladized charcoal Va absorbed only up to 1 mole of hydrogen instead of 2 moles, so that the preparation of 2-hydrazino-4-methyl-thiazol could not be realized in this way.

This lack of success prompted us to synthesize 2(2′-benzylhydrazino)-4-methyl-thiazol (type Va) from benzyl-hydrazine *via* 1-benzyl-thiosemicarbazide VIII. Condensation of thiosemicarbazide itself with a chloro ketone was not attempted as the formation of thiodiazines in similar reactions could never be avoided (17). This thiosemicarbazide showed a higher melting point than its 2-benzyl isomer (IX) (18) and did not react with benzaldehyde, supporting structure VIII. The well known thermic rearrangement of 1-substituted thiosemicarbazides into 2-substituted derivatives can in our opinion rather be explained by assuming a migration of the thiocarbaminyl i. e. acyl group, than by a shift of an aryl, resp. aralkyl radical.

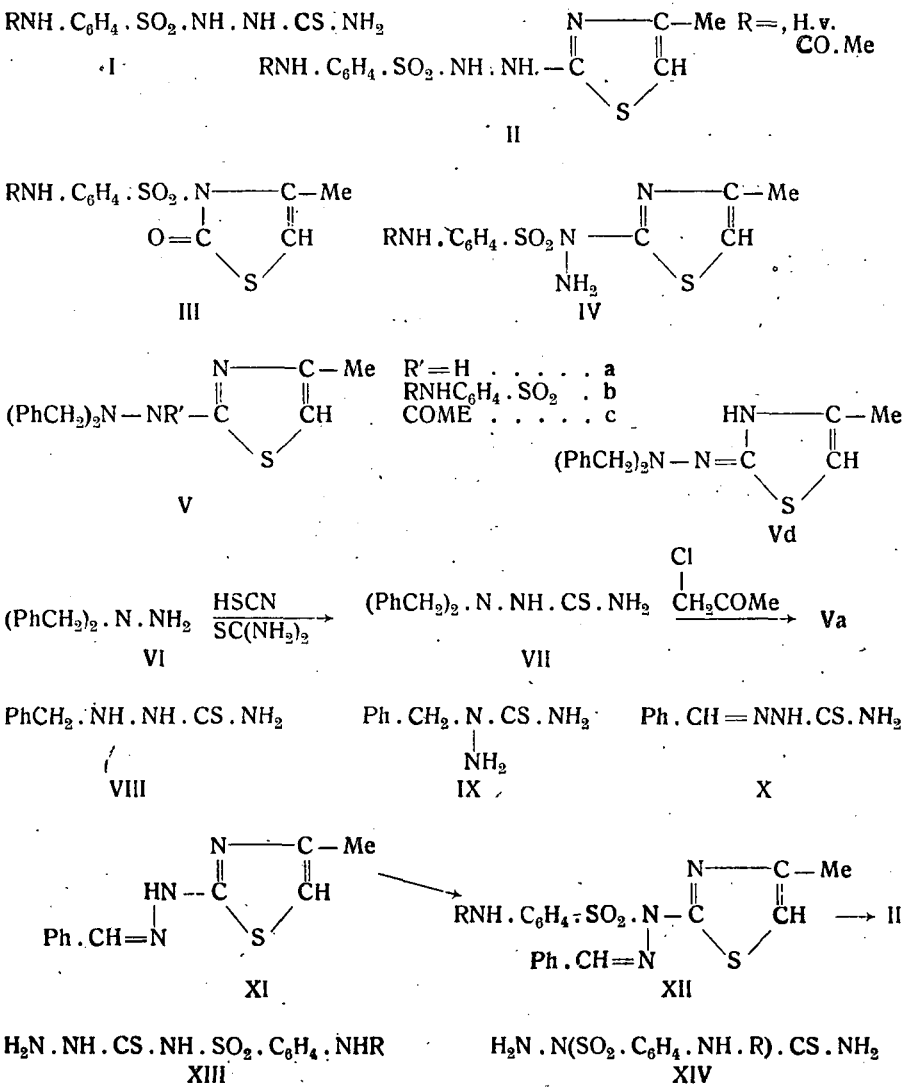
The crystalline 2(2′-benzyl-hydrazino)-4-methyl thiazol was obtained smoothly from VIII with monochloro acetone; it could be acylated with benzene sulfonyl chloride, as elimination of a benzyl group from Va resulted obviously in an abolition of steric hindrance. However, neither the base, nor its acyl derivative were able to undergo hydrogenolysis. This failure can be attributed to the formation of a sulphur containing catalyst poison, or to a relatively great stability of the benzyl group at the nitrogen.

We succeeded finally in synthesizing the required derivatives of 2-hydrazino thiazol, starting with benzal-thiosemicarbazide (X) (19). Its condensation with monochloro acetone gave the 2′-benzal derivative of 2-hydrazino-4-methyl-thiazol (XI) with a very good yield. This compound is very resistant towards acid hydrolysis. It could be acylated by means of acetyl-sulfanilyl chloride in pyridine yielding 2(2′-benzal-1′-acetylsulfanilyl-hydrazino)-4-methyl-thiazol (XII) (benzalderivative of IV). XII is insoluble in alkali, supporting the correctness of this formula.

Simultaneous removal of the benzal and acetyl groups by acid hydrolysis gave a crystalline compound with the analytical data calculated for the expected 2-(sulfanilyl-hydrazino)-4-methyl-thiazol. IV. However, it is readily soluble in diluted acids and alkalis. This amphoteric character can only be explained by suggesting for it structure II, of the isomeric 2′-sulfanilyl derivative. This interesting example of the migration of an arylsulfonyl group will be investigated more intensively later.

Another synthesis of II was attempted by allowing acetyl-sulfanilyl-thiosemicarbazide I to react with monochloro acetone. Analytical data of the obtained crystalline product as well as its neutral character suggest the structure of 3-acetyl-sulfanilyl-4-methyl-thiazolon-2 (III). Its formation can be explained in 2 ways either by assuming structure of 4-acetylsulfanilyl-thiosemicarbazide

for the starting material, and subsequent hydrolysis of the primarily formed 3-acetylsulfanilyl-4-methyl-thiazolon-2-hydrazone, or by supposing migration of the arylsulfonyl group of 2(2'-acetylsulfanilyl--hydrazino)-4-methyl-thiazol to the nitrogen at position 3 of the thiazol ring, with subsequent hydrolytic splitting off of hydrazine. As in our experiments acetylsulfanilyl thiosemicarbazide did not react



with benzaldehyde, a primary amino group, as in the case of XIII can not be present. Since acetylsulfanilyl thiosemicarbazide is easily soluble in dilute alkali, the possibility of a structure like XIV can also be regarded as very improbable. Consequently, acetylsulfanilyl thiosemicarbazide possesses structure I. so that the first assumption can be disregarded in favor of the second one.

This observation is surprising as similar *intra*molecular migration of an arylsulfonyl radical has not yet been reported. *Inter*molecular migration of an arylsulfonyl group from the ring nitrogen of some 2-acylimido-3-acyl-thiazolons to the amino nitrogen of amino-thiazol have already been described (16).

Rearrangement of IV to IIb, resp. conversion of I to III. will be the subject of systematic investigations.

Domagk (20) recorded recently on the strong tuberculostatic action of benzaldehyde thiosemicarbazon. In this regard compound XI can also receive some attention as it is to investigate, whether ring closure of benzaldehyde thiosemicarbazon to XI effect enhancement or diminution of the antibacterial activity. XI, and 2-sulfanilylhydrazino-4-methyl-thiazol will be assayed by Prof. G. Iványovics for antibacterial, especially for tuberculostatic activity.

* * *

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Summary.

Several attempts were made for the synthesis of sulfanilyl-hydrazino-methyl-thiazols. 2(2'-Sulfanilylhydrazino)-4-methyl-thiazol II was synthesized starting from benzaldehyde thiosemicarbazon *via* XI → IVa. Acid hydrolysis of the protecting benzal group from the primary hydrazino group effected a simultaneous shift of the arylsulfonyl radical from the secondary aminogroup to the liberated primary amino group. Condensation of acetylsulfanilyl thiosemicarbazide with monochloro acetone caused splitting off of hydrazine. XI and II may receive attention as antibacterials, their bioassay is in progress.

Experimental.

Benzyl hydrazine. 91 g. (0.44 mole) of benzaldazine were dissolved under stirring in 76 ml. (1.52 mole) of hot hydrazine hydrate. The solution was cooled back, extracted with a total of 250 ml. of ether, the solvent blown off, the residual (94.8 g.) oil distilled b. p. 92—104° (1 mm). Yield, 72 g. of benzal hydrazine. 36 g. (0.30 mole) of this product were hydrogenated in 250 ml. of alcohol with 1 g. Pd- charcoal (20% Pd), the uptake of hydrogene stopped after absorption of 8660 ml., i. e. 7680 n-ml (calcd. 6726 ml.). The solution was then evaporated and the remainder distilled, b. p. 80—81.5° (1.4 mm.), yield, 10.1 g. benzyl hydrazine, which has been converted into 14.8 g. of the hydrochloride, m. p. 148°.

Anal. Calcd. for $C_7H_{10}N_2$ 2HCl : Cl, 36.5; Found: Cl, 36.2.

1-Benzyl-thiosemicarbazide (VIII). 14.1 g. (0.07 mole) of the hydrochloride obtained above were dissolved in 15 ml. of water, 32.8 ml. of 2.1 N-sodium hydroxide (0.07 mole) solution then 7 g. (0.07 mole) of potassium thiocyanate were added and the whole boiled for 2 hours. Water was removed, the residue extracted by boiling four time with a total of 400 ml. of ethyl acetate. On cooling 1.4 g. of crystals separated, m. p. 175°; the residue of the solution (9.5 g.) showed the same m. p.

Anal. Calcd. for $C_8H_{11}N_3S$: S, 17.7. Found: S, 17.5.

2-2'-Benzylhydrazino-4-methyl thiazol. 1.81 g. (0.01 mole) of 1-benzylthiosemicarbazide in 10 ml. of 50% ethanol was condensed with 0.95 ml. monochloroacetone (0.01 mole) by refluxing for two hours. The solvent was then removed,

the sticky residue (2.9 g.) converted into the picrate, yield, 3.5 g. (78%). m. p. 135—136°, which raised on recrystallisation from ethanol to 143°. 1.7 g. of this picrate were treated with 2N-sodium hydroxide, the free base extracted with ether, yield, 0.6 g. thiazol derivative m. p. 44°.

Anal. Calcd. for $C_{11}H_{13}N_3S$: N, 19.2; S, 14.6. Found: N. 19.4; S, 14.5.

1.1-Dibenzyl-hydrazine (VI), was prepared according to *Busch* and *Weiss* (13), but some changes were undertaken to which we shall refer below. 156.2 g. (3.12 mole) of hydrazin hydrate was diluted with a mechanical stirrer, thermometer, dropping funnel and reflux condenser. Then 200 g. (1.58 mole) of benzyl chloride in 1 L. ethanol were added drop by drop under stirring in 40 min, meanwhile the temperature was maintained at 50°, and the whole refluxed for 2 hours under stirring. The solvent (870 ml.) was distilled off, the residue cooled in an ice-salt mixture. The separated crystals (consisting of the hydrochlorides of dibenzylhydrazine and of hydrazine) were collected on a filter, washed with some ice-cold alcohol and dried in a desiccator, yield, 87 g. Treatment with alkali afforded 41 g. of pure dibenzyl hydrazine. The filtrate was diluted with 500 ml. water, and extracted twice with a total of 800 ml. of ether, the dried ether solution was concentrated to a small volume, treated with 200 ml. of 15% hydrogene chloride in alcohol, yield, 70 g., m. p. 180° (not sharp). *Busch* suggested for this substance to be dibenzyl hydrazine bis-hydrochloride. We found, however, that always a mixture of hydrazine hydrochloride with the monohydrochloride of dibenzyl hydrazine was present. This assumption was proved by treatment of the product with alkali, when only a part of the calculated amount of dibenzyl hydrazine could be obtained, on the other hand by treatment of pure as-dibenzyl hydrazine even with a great excess of alcoholic HCl, only the mono-hydrochloride was formed. *Kenner* and *Wilson* also reported (13) the formation of the monohydrochloride. 1.1-Dibenzylhydrazine yield, 60% (calculated upon benzyl chloride used); m. p. 65°.

Anal. Calcd. for $C_{14}H_{16}N_2$: N, 13.2. Found: N, 13.5.

1.1-Dibenzyl-thiosemicarbazide. (VII.) *a. From 1.1-dibenzyl hydrazine.* A solution of 4.6 g. (0.019 mole) of 1.1-dibenzyl hydrazine monohydrochloride and 2.3 g. (0023 mole) of potassium thiocyanate was refluxed for 12 hours, the alcohol evaporated, the residue taken up in 200 ml. of ethyl acetate, washed with 50 ml. of water then with 73 ml. of 1% hydrochloric acid (to remove dibenzylhydrazine, as dibenzyl thiosemicarbazide is insoluble in such a dilute acid.) Ethyl acetate was blown off, to give 3.6 g. of an yellowish oil which gave on treatment with hydrogen chloride in ethyl acetate, a hydrochloride. The base is sufficiently pure for transformation into the thiazol derivate.

Anal. Calcd. for $C_{35}H_{18}N_3SCl$: N, 13.6. Found: N, 12.9.

b) From thiocarbamide. A mixture of 0.75 g. (0.01 mole) of thiocarbomide and of 2.1 g. (0.01 mole) of 1.1-dibenzyl hydrazine was heated to 160° for three hours, a vigorous evolution of ammonia was observed. The sirupy residue weighed 2.75 g; this was extracted with boiling petroleum ether, then dissolved in 50 ml. of ethyl acetate, washed with two portions of N/2 hydrochloric acid, then evaporated. This oil, 1.4 g. (51.9% calcd. upon the amount of dibenzyl hydrazine) gave approximately the expected analytical data. Calcd. S, 11.8. Found: S, 13.6. It is satisfactorily pure for condensation reaction.

c) The best method leading to 1.1-dibenzyl-thiosemicarbazide was the *rearrangement of dibenzyl hydrazine thiocyanate* in aqueous alcoholic solution, as follows: A mixture of 54 g. (0.22 mole) of 1.1-dibenzyl hydrazine monohydrochloride, 250 ml. of alcohol, 41 g. (0.42 mole) of potassium thiocyanate and 50 ml. of water was heated for 12 hours in a steam bath, the solvent evaporated

and the residue worked up as described under a.) Yield, 39.4 g. (67.6%) of a pale-yellow colored oil.

Anal. Calcd. for $C_{35}H_{17}N_3S$: S, 11.8. Found: S, 12.6.

2-(2'.2'-Dibenzyl-hydrazino)-4-methyl-thiazol. (Va.) a) From 1.1-Dibenzyl-thiosemicarbazide. A solution of 40.4 g. (0.15 mole) of crude 1.1-dibenzyl-thiosemicarbazide and of 13.8 g. (0.15 mole) of monochloro acetone in 200 ml of ethanol (96%) was refluxed for two hours, the solvent evaporated, the residual amorphous mass weighed 45.5 g. Then 300 ml. of a concentrated alcoholic solution of picric acid was added. Its yellow colored picrate (48 g.) showed m. p. 190°; the mother liquor furnished a further crop, 16.3 g. melting from 145 till 155°. The first portion obtained was dissolved in 300 ml. of chloroform, washed three times with a total of 350 ml. of 3% sodium hydroxide, dried and the solvent removed. Yield, 18.3 g. of colourless crystals of the thiazol derivative, m. p. 158—159°.

Anal. Calcd. for $C_{18}H_{19}N_3S$: N, 13.6; S, 10.4. Found: N, 13.55; S, 10.3.

The second crop of picrate gave, after recrystallisation from alcohol and subsequent alkaline treatment further 3.8 g. of the pure hydrazino-thiazol derivative. Total yield, 22.1 g (49%).

b) A solution of 4.57 g. (0.039 mole) of thiocyano acetone (14) and of 8.35 g. (0.039 mole) of 1.1-dibenzyl hydrazine in 15 ml. of ethanol was refluxed for an hour, the brownish coloured solution evaporated to dryness, the residue taken up in chloroform, washed with water, evaporated, then converted into the picrate as reported in the previous experiment to furnish 3.55 g. of a picrate m. p. 185° (after recrystallisation yield 2.5 g.) From this 1.5 g. of the pure hydrazino thiazol derivative could be secured.

2-(1'-Acetyl-2'.2'-dibenzylhydrazino)-4-methyl-thiazol (Vc.) Treatment of 1.04 g. (0.0034 mole) of dibenzyl hydrazino-4-methyl-thiazol in 3 ml. dry pyridine with 1 ml. of acetic anhydride (0.011 mole) furnished in the usual manner 0.95 g. (83%) of the acetyl derivative, m. p. 90°, (after recrystallisation from 25 ml. of 90% methanol.)

Anal. Calcd. for $C_{20}H_{21}ON_3S$: N, 11.95. Found: N, 12.1.

2(2'-benzalhydrazino)-4-methyl-thiazol. (XI.) Forty-six grams of benzaldehyde thiosemicarbazon were dissolved in 184 ml. of acetone and 23 ml. of monochloro acetone added, the mixture refluxed for an hour. The *hydrochloride* of the thiazol derivative separates soon, forming colorless prisms. Yield, 47.5 g; m. p. 186—187° (dec.). Recrystallisation from alkohol-acetone furnish a product, m. p. 193° (dec.). It is very resistant towards acid hydrolysis. Boiling with conc. HCl after cooling the hydrazine derivative was recovered.

Anal. Calcd. for $C_{11}H_{11}N_3S$. HCl : N, 16.55; Found, N, 16.81.

The *base* was liberated by dissolving 25.3 g. hydrochloride in 200 ml of hot methanol and adding 20 ml. of 5N NaOH in abs. methanol. A part crystallizes immediately, another on addition of 500 ml. of water. The base yielded long needles (from alcohol), m. p. 190°.

Anal. Calc. for $C_{11}H_{11}N_3S$: C, 60.79; H, 5.11; N, 19.35.
Found: C, 60.53; H, 5.32; N, 19.16.

2(1'-acetylsulfanilyl-2'-benzal-hydrazino)-4-methyl-thiazol. (XII). Thirteen and half grams of the pure benzal derivative (X) were dissolved in 60 ml. hot pyridine, then 16 g. acetylsulfanilyl chloride added and the reaction mixture heated for an hour in a steam bath. It was then poured into 200 ml. of 5% sulfuric acid, the oily precipitate became suddenly crystalline. Yield, 20 g. of a brown colored solid. Repeated recrystallization from alcohol afforded 5.1 g. of nearly colorless plates; m. p. 171—172°. Insoluble in alkali.

Anal. Calc. for $C_{19}H_{18}O_3N_4S_2$: C, 55.05; H, 4.35; S, 15.5.
Found: C, 54.90; H, 4.82; S, 14.06, 14.0.

2(2'-Sulfanilyl-hydrazino)-4-methyl-thiazol. Two grams of the acetylsulfanilyl-benzal derivative, mentioned above, was dissolved in 20 ml. of hot 2N hydrochloric acid and refluxed for an hour. The odor of benzaldehyde became soon remarkable, simultaneously oily drops appeared. Finally charcoal was added and the solution filtered. The filtrate gives on addition of alkali a precipitate which redissolves in an excess of alkali. Ammonia afforded a violet colored solution and a dark colored precipitate. The free base could be obtained by neutralizing the solution with solid sodium bicarbonate. Yield, 0.5 g., m. p. 153—155° (dec.). It is easily soluble in dilute hydrochloric acid and in N. sodium hydroxide, in alcohol, ethyl acetate, slightly soluble in water, insoluble in benzene.

Anal. Calc. for $C_{10}H_{12}O_2N_4S_2$: N, 18.7. Found: N, 18.2.

The *bis-hydrochloride* formed by adding alcoholic hydrogene chloride to the free base. M. p.: over 225°, it decomposes slowly, without melting. It is very soluble in water.

Anal. Calc. for $C_{10}H_{12}N_4O_2S_2 \cdot 2HCl$: Cl, 19.9. Found: Cl, 19.4.

Condensation of 1-acetylsulfanilyl-thiosemicarbazide with monochloro acetone.

Acetylsulfanilyl thiosemicarbazide was prepared according to Roth and Degering (3). It is easily soluble in 2N sodium hydroxide and did not give any precipitate with benzaldehyde. It is therefore neither a 2- nor a 4-acyl derivative.

1. Twenty and six tenth grams of acetylsulfanilyl thiosemicarbazide were heated in a steam bath with 6.7 g. of monochloro acetone and with 12 g. of dry pyridine for an hour. The product was then poured into water which was acidified previously with sulfuric acid. The oily precipitate solidified on triturating with dilute sulfuric acid. Yield, 20 g of dark brown crystals. Recrystallization from 90 ml. of 80% acetone and repeated recrystallization of the product thus obtained afforded 6.7 g. delicate white needles, m. p. 185°. Mixed m. p. with the starting material: 160—175°. It is insoluble in alkali, soluble in hot 20% sulfuric acid.

Anal. Calc. for $C_{12}H_{12}O_4N_2S_2$ (III) : N, 8.97; S. 20.05. Found: N, 8.91, 8.67; S, 19.70.

2. The same product was obtained by heating 2.3 g. I with 0.92 g. of monochloro acetone in 4 ml. of dry pyridine for an hour. Yield, 2.2 g., m. p. 186°, in part 214°. Recrystallization from 80% acetone furnished 1.2 g. colorless crystals, m. p 184—185°, and a further crop, 0.3 g., m. p. 174—177°.

Attempted reduction of diazotized 2-amino-4-methyl-thiazol.

a) A solution obtained by diazotization from 11.4 g. of 2-amino-4-methyl-thiazol in hydrochloric acid solution was treated with 31.5 g. of sodium sulfite according to the preparation of phenylhydrazine (21), but only the sodium salt of an organic sulfonic acid could be separated instead of the expected hydrazine derivative.

b) The solution of the diazonium salt obtained above was treated with a solution of 280 g. stannous chloride in hydrochloric acid at 0°. After stirring for 4 hours a white solid precipitated which contained 24.5% Cl. It was then treated with excess alkali and in turn extracted with chloroform. The resulting oily basic substance was identified 1.) by converting with p-acetamino-benzene-sulfonyl chloride in pyridine into the corresponding acylderivative, m. p. 255°, identical with acetylsulfanilyl-2-amino-4-methyl-thiazol (12). 2.) By converting

with picric acid into the picrate, m. p. 230—232° (11) of the starting material. This latter was analysed:

Anal. Calc. for $C_{10}H_9O_7N_5S$: N, 20.9, Found: N, 20.6.

Acknowledgement. The author is indebted to the Analytical Department of the Chinoin Manufactory and to Miss M. Kovács Oskolás for carrying out the analyses.

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On the magnetic properties of the $CoCl_2$—H_2O—HCl system.

(Preliminary communication)

by P. F. Váradi

The change in colour of the watery solution of $CoCl_2$ effected by different materials, is a problem several times discussed. The elements of the transition group (Fe, Co, Ni) are occupying an interesting place in the periodical system because of their magnetic properties. Several authors determined the magnetic properties, of their compounds, in solution too (1a). Meanwhile they found only a qualitative connection between colour and magnetic data. Fahlenbrach (2) searched the magnetic susceptibility of $CoCl_2$ in pure water, pyridin and aethylacohol, he found, that red colour and high susceptibility belong to low temperature, while to high temperature blue colour and low susceptibility. Here the change in colour has taken place by the increasing of the temperature.

I determined during my experiments the magnetic susceptibility of $CoCl_2$ in H_2O—HCl solution. I kept constant the $CoCl_2$ (0·04577 mol) and changed the HCl concentration, so I could vary on constant temperature — depending only on the HCl amount — the colour of the solution, from red to dark blue. To the measureing of the magnetic susceptibility of the different coloured solutions I used the cylindrical method, what Klemm (4) recommended (and which they call also the method of Plücker (8) or of Gouy (3)). I enlarged it with the varying of the field-force recommended by McLennan, Ruedy, Cohen (5). Then I altered only a few things on the method. I counted the susceptibility of the solution according to the advice of Klemm (4) applied to this method. And with the Wiedemann (9) thesis the susceptibility of the solved salt:

$$x_{SO} = p\,x_S + (1-p)\,x_{SV}$$

Where x_{SO} means the gr. susceptibility of the solution, x_S of the salt, x_{SV} of the solvent, and p means the mass concentration of the salt. From this

$$x_S = \frac{100}{p'}\,\sigma\,(x_{SO} - x_{SV}) + x_{SV}$$

here σ means the density of the liquid, and p' the gr-s of the salt in 100 ccm.

Materials: pro anal. (Ni free) $CoCl_2 . 6H_2O$ Merck fabrication, twice destilled water from Jenaer glass, and pro anal. (free from iron) HCl. I prepared the solutions always in the same manner. I let it stand for a day. I determined the $CoCl_2$ concentration

by the method of Brode (1). I carried out my experiments always at a constant temperature (17° C ± 1° C).

Fig. 1. represents my results. Here the concentration of the $CoCl_2$ and temperature of the solutions is always constant, and the HCl concentration in % is plotted against the $1/x \cdot 10^{-2}$ values. The colour of the solution is changing from left to right, from red to dark blue. The values of the pure watery solution are in conformity with the results of different authors, while the results of the dark blue solution are giving back the susceptibilities of other blue as concentrated $CoCl_2$ solutions (2). In my values — out of my experimental arrangement — the fault is ± 5%.

The evaluation of my results led in two directions. The first is the behavior of the cobalto complexes, which are forming in the $CoCl_2 - H_2O - HCl$ system in magnetic field, the second is the composition of these complexes.

On the base of my experiments for all we can state, that the $CoCl_2$ solved in $H_2O - HCl$ behaves always paramagnetic,

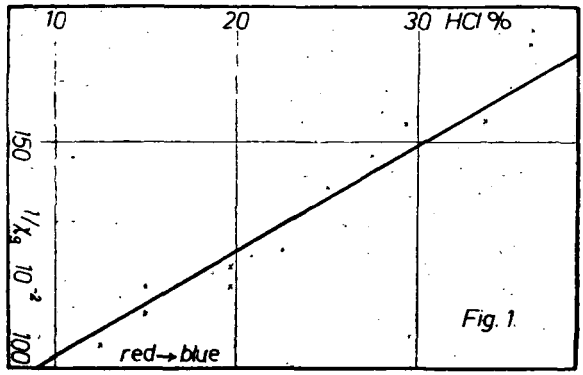

Fig. 1.

and the susceptibilities of those between the measuring limits (4900—5700 gauss) are independent from the field-force. It could be stated also from my results, that the magnetic susceptibility of the $CoCl_2$ is decreasing by increasing the HCl concentration. Its reason is that by increasing the amount of HCl is developing such a paramagnetic cobalto complex, whose susceptibility is smaller, and independent from the field-force between the measuring limits.

On the base of the researches made up to the present (4a, 10) in watery and not watery blue solution of the $CoCl_2$ we have to suggest the presence of $CoCl_4^{--}$ complex ion whose structure however could not be cleared up alone with spectroscopy. Therefore I attempted to clear up the structure and electron distribution of the cobalto complexes developing in the $CoCl_2 - H_2O -$ HCl system, with magnetic experiments. Klemm's work (4) says only generality about the relation between magnetic properties and molecule structure of solved materials. He remarks that to clear up such a problem in every case some other physico-chemical (spectroscopical!) experiments are needed. Pauling worked out a theory (6, 7) between the magnetic properties and electron

distribution of the componunds. By the interpretation of my results I am to rely on Pauling's works. On the base of his works I can state from my results that by increasing the HCl concentration there is beginning the hegemony of the tetrahedral cobalto complexes with a coordination number of four. It can also be said, that in the $CoCl_4^{--}$ complex rather electronpair bonds are forming than electrostatical. To the $Co(H_2O)_6^{++}$ complex, developing in the red coloured solution, I obtained the result, that the water molecules are producing a strong ion-dipol or a bond type between the ion-dipol and semipolar. Other intermediary compounds and their structure could not be cleard up by measuring the magnetic properties. To solve this problem too, I shall determine the absorption spectrum of the solution in the visible spectrum whose magnetochemical properties I have already measured.

With temperature and with the spectroscopical measuring I am the temperature and with the spectroscopical measuring I am continuing my work.

Here I wish to extend my sincere thanks to Prof. Á Kiss director of the Institute of Inorganic and Anal. Chemistry, who has ever been a great help in my works with his constant suggestions. Meanwhile I express my gratitude to Prof. P. Fröhlich director of the Institute of Experimental Physics, and to assistant dr. L. Szalay who were kind enough to let me have the necessary instruments and thereby rendering my work possible.

Szeged 10 2 1949

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Intensities in Molecular Spectra.

by R. Pauncz.

(Received January 1949.)

Introduction. Mulliken in his most interesting papers (1) made a serious attempt to interprete the intensities in molecular spectra on the quantum mechanical basis. His calculations were made in most cases with aid of the molecular orbital (MO) method.

The aim of this and subsequent papers is to treat the same problem by means of other quantum mechanical approximations. We shall compare the calculated values with the empirical ones and the accordance or deviation will serve as indicator for the degree of approximation by the method employed.

The Oscillator Strength. We shall use the method described by Mulliken (1) comparing the calculated and the observed oscillator strength.

In order to obtain the calculated oscillator strength, f_{calc} we compute the dipole strength $D = Q^2$ (cf. II. 1) by means of the quantum mechanical Ψ functions describing the molecular states and from this

$$f_{calc} = 1{\cdot}096 \,.\, 10^{11} \,.\, Q^2 \,.\, \nu \qquad (1)$$

where ν is the place of the absorption maximum in cm^{-1}.

On the other hand we get the observed oscillator strength f_{obs} from the empirical absorption curve by means of the relation

$$f_{obs} = 4{\cdot}32 \,.\, 10^{-9} \,.\, \int \varepsilon_\nu d\nu \approx 4 \,.\, 32 \,.\, 10^{-9} \,.\, \varepsilon^{max} \,.\, \Delta\nu \qquad (2)$$

in which $\Delta\nu$ is the half width of the band, ε the molar absorption coefficient.

The theoretically computed f_{calc} value refers to the gaseous state. In the case of solution we must made a correction due to the Lorenz-Lorentz forces. However some investigations (2) have shown that the agreement is better, when this correction is omitted.

Since the individual approximate methods treat the problem from different point of view and from the comparisons we will draw conclusions with respect to the method itself, we must make known by each the starting-point, the assumption and the simplifications used by the method.

In this paper we shall investigate the intensities in molecular spectra with aid of the Slater-Pauling method.

I. *The Outline of the Slater-Pauling Method.*

1. *Starting point, assumptions (Heitler-London).* We shall investigate in the following only organic compounds in which the number of π electrons is equal to the number of C atoms forming the skeleton of the molecule. The electron cloud of each π electron forms a dumb bell the axis of which being perpendicular to the plane of the molecule, therefore it does not appreciably overlap with the σ electrons, the electron cloud of the latter being rotation-symmetrical around the joining line of two adjacent atoms.

The π electrons are less firmly bound than the σ electrons They are responsible for many physical properties of the molecule among them for the visible and ultraviolet spectra. Investigating the intensity problem of the spectrum, we must only deal with the π electrons.

In the case of n C atoms and n π electrons, we have an n electron problem what cannot be solved rigorously quantum mechanically. We must make some simplifications to get a first order approximation.

The idea of this simplification is due to Heitler and London and is the same as in the case of the hydrogen molecule. We think the atoms very far from each other, *one π electron being by each atom* (that is we exclude the ionic, polar cases in which two electrons are by one atom). We suppose that in this approximation only this atom acts upon the electron, in other words we take as perturbation the action of the other atoms and electrons.

In this approximation Schrödinger's equation is separable in n one-electron-problems and the solution is the product of n one-electron-functions: $\psi = a\,(1)\,.\,b\,(2)\,.\,c\,(3)\ldots$ (1, 2,... denote the coordinatetriple of the first, second,... electron, a, b,... mean the solution of the one-electron-problem by the first, second,... atom.)

However the problem is a degenerate one because all the functions, which differ from the above mentioned only in the arbitrary permutation of the electrons among the atoms (e. g. $\psi = a\,(2)\,.\,b\,(1)\,.\,c\,(3)\ldots$) belong to the same energy. We have $n!$ such functions.

When we treat the problem with aid of the perturbation theory introducing the interaction of the electrons as perturbation, we take these $n!$ functions as of zero order approximation and we look for such linear combinations of them which approximate better the real states of the molecule.

The determination of these coefficients, which are necessary to the linear combination, requires the solution of a linear system of equations set up in taking account of the perturbation. This is possible only in the case when the determinant of the system vanishes. The roots of this so called *secular determinant* give the possible energy values of the perturbed system.

In this case the equation system consists of $n!$ equations, the secular determinant has $n!$ rows, the degree of the secular equation is $n!$. This is a very great number (e. g. in the case of benzene $n = 6, n! = 720$) to deal with it.

2. *The Slater Method.* Slater achieved a very great simplifica-

tion of the problem introducing the spin variable and taking account of Pauli's exclusion principle. (3)

Neglecting the magnetic interactions we can write the one-electron-function as a product: $\Psi(x, y, z, m_s) = u(x, y, z) \cdot \sigma(m_s)$ of two functions where u depends only upon the three space coordinates and σ only upon the spin coordinate (m) The latter is the z component of the spin of the electron and can assume only two values: $m = +1/2, m = -1/2$ (measured in $h/2\pi$ units).

The u function measures the probability to find the electron in the x, y, z place, the σ function measures the probability to find the z component of the spin of the electron (m) with the values $+1/2$ and $-1/2$, respectively.

When the electron spin has the value $+1/2$, then the values of the σ function are: α { for $m_s = +1/2$ $\sigma(m_s) = 1$ (certainty); for $m_s = -1/2$ $\sigma(m_s) = 0$

When the electron spin has the value $-1/2$, then the values of the σ function are: β { for $m_s = +1/2$ $\sigma(m_s) = 0$; for $m_s = -1/2$ $\sigma(m_s) = 1$ (certainty)

We call these functions α and β, respectively. It follows from their definition that α and β are mutually orthogonal:

$$\alpha(+1/2) \cdot \beta(+1/2) + \alpha(-1/2) \cdot \beta(-1/2) = 0 \qquad (3)$$

and they are normalized

$$\alpha^2(+1/2) + \alpha^2(-1/2) = 1 \qquad (4)$$

This is a very important fact by the calculation of the dipole strength integral.

Slater takes into account Pauli's exclusion principle using only wave functions antisymmetrized in the electrons. These functions must be written in determinant form or in the equivalent sum of permutations taking with + or — sign according to even or odd permutation. We denote these Slater functions by the following equivalent formulae:

Slater function

(e. g. in the case of four electrons one Slater function)

$$\varphi = \frac{1}{\sqrt{4!}} \begin{vmatrix} a(1)\alpha(1) & a(2)\alpha(2) & a(3)\alpha(3) & a(4)\alpha(4) \\ b(1)\alpha(1) & b(2)\alpha(2) & b(3)\alpha(3) & b(4)\alpha(4) \\ c(1)\beta(1) & c(2)\beta(2) & c(3)\beta(3) & c(4)\beta(4) \\ d(1)\alpha(1) & d(2)\alpha(2) & d(3)\alpha(3) & d(4)\alpha(4) \end{vmatrix} \qquad (5a)$$

$$\varphi = \frac{1}{\sqrt{4!}} \sum_P (-1)^P P\, a(1)\alpha(1) \cdot b(2)\alpha(2) \cdot c(3)\beta(3) \cdot d(4)\alpha(4) \qquad (5b)$$

$$\varphi = \frac{1}{\sqrt{4!}} \begin{pmatrix} a & b & c & d \\ \alpha & \alpha & \beta & \alpha \end{pmatrix} \qquad (5c)$$

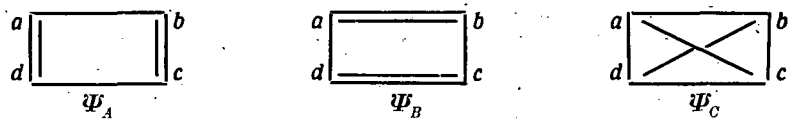
(P means the permutation of the electrons $(1, 2, \ldots)$ among the atoms. This function corresponds to the spin state, when the electrons by the first, second, third and fourth atom, respectively have the spinvalues $+1/2, +1/2, -1/2$, and $+1/2$, respectively.)

We can form 2^n such functions because by each atom the spin can assume two values. That means that the degree of the secular equation is reduced from $n!$ to 2^n. (e. g. by benzene from 720 to 64).

Slater obtained a further simplification proving that by the linear combination we must use only functions by which the resultant spin has the same component on the z axis, or in other words which have the same number α and β. The secular equation is dissolved in equations of minor degree. (e. g. in the case of benzene in equations of $1, 6, 15, 20, 15, 6, 1$ degree, corresponding to the cases that the resultant spin has the following components: $3, 2, 1, 0, -1, -2, -3$.) This is the method used by Hückel treating the benzene problem in his first paper (4).

3. *The vector-bond method (Eyring, Pauling).* In the next step it was demonstrated (5) that in the linear combination one must use only functions by which the resultant spin has the same value *(not only his z component)* In classifying the states corresponding to these functions, we get singlet (resultant spin $= 0$), triplet (resultant spin $= 1$) and so on, states. The functions can be obtained from the Slater functions by means of the vector-bond diagrams.

Let us consider for example the singlet states. The resultant spin is 0. Connecting with bonds the atoms by which the spin is compensated ($-1/2$ —— $+1/2$) we obtain many figures which are called vector-bond diagrams. (E. g. in the case of four atoms we can obtain the following three diagrams):



Each diagram is to obtained from Slater functions (spin states) which are consistent with the figure. When we draw an arrow from the atom by which the electron spin is $-1/2$, to atom by which it is $+1/2$, we obtain, e. g. the first diagram as a sum of four Slater functions (spin states):

$$\Psi_A = \begin{matrix} a \\ d \end{matrix}\boxed{}\begin{matrix} b \\ c \end{matrix} = + \begin{matrix} a \\ d \end{matrix}\boxed{\uparrow\uparrow}\begin{matrix} b \\ c \end{matrix} - \begin{matrix} a \\ d \end{matrix}\boxed{\downarrow\uparrow}\begin{matrix} b \\ c \end{matrix} + \begin{matrix} a \\ d \end{matrix}\boxed{\downarrow\downarrow}\begin{matrix} b \\ c \end{matrix} - \begin{matrix} a \\ d \end{matrix}\boxed{\uparrow\downarrow}\begin{matrix} b \\ c \end{matrix}$$

$$\Psi_A = \frac{1}{\sqrt{4!}}\left\{\begin{pmatrix} a & b & c & d \\ \alpha & \alpha & \beta & \beta \end{pmatrix} - \begin{pmatrix} a & b & c & d \\ \beta & \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} a & b & c & d \\ \beta & \beta & \alpha & \alpha \end{pmatrix} - \begin{pmatrix} a & b & c & d \\ \alpha & \beta & \alpha & \beta \end{pmatrix}\right\}$$

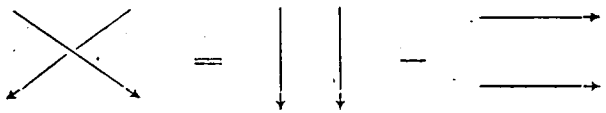
$$\Psi_A = + \varphi_{\mathrm{I}} - \varphi_{\mathrm{II}} + \varphi_{\mathrm{III}} - \varphi_{\mathrm{IV}}$$

(taking with $+$ or $-$ sign according to even or odd reverse of the arrows with respect to the first Slater function φ_1)

Rumer pointed out (6) that the functions corresponding to the vector-bond diagrams are not all linearly independent. According to his considerations we obtain the independent ones, writing the atoms on the circumference of a circle and forming all the possible vector-bond diagrams by which no two bond intersects each other. These are called *canonical structures* by Pauling (7)

(e. g. by the example mentioned above, only two are canonical, i. e. independent: Ψ_A and Ψ_B)

The other vector-bond diagrams can be resolved in the uncrossed ones by the repeated use of the following rule:



(6)

By the determination of the coefficients we must use only the independent set i. e. the canonical structures. This means that the secular determinant is further reduced. (e. g. by the benzene there are five linearly independent, canonical structures for the singlet state and we must solve an equation of the 5. degree

The real states of the molecule can be approximated by the linear composition of these five structures. The lowest state has less energy than any of the five structures according to the quantum mechanical perturbation computations.

After Pauling's comment this is due to the „resonance' among the five structures. (7)

4. *Vector-bond method and mesomerism.* It is a close connection between these vector-bond (VB) functions derived on the basis of the quantum mechanics and the mesomeric structures introduced by the theoretical chemistry.

The two methods give the same conclusion referring to the stabilization of the molecule because of the resonance among the mesomeric (canonical) structures.

The difference between them is, that the mesomerism theory gives only qualitative conclusions, but the Slater-Pauling treatment makes possible the evaluation of many physical and chemical properties of the molecule. — In the following treatment we shall use for the evaluation of intensity of spectrum.

II. *Intensity calculations according to S—P method.*

1. *The dipole strength.*

$$Q^2 = Q_x^2 + Q_y^2 + Q_z^2$$

In order to get the x component of the dipole strength Q_x, from a molecular state characterized by the function Ψ_i to other molecular states characterized by the functions $\Psi_I, \Psi_{II}, \ldots, \Psi_k$ (Q_x is proportional to the *probability of transition* from the state Ψ_i to states $\Psi_I, \Psi_{II} \ldots$, under the emission or absorption of light quanta polarized along the x axis), we must form the following product: $X\Psi_i \left(X = \sum_\nu x_\nu\right)$ x_ν means the x coordinate of the ν-th electron) and expand in terms of the functions, $\Psi_I, \Psi_{II}, \ldots$ as follows:

$$X\Psi_i = c_{i1}\Psi_I + c_{i2}\Psi_{II} + c_{i3}\Psi_{III} + \ldots \qquad (7)$$

The coefficient c_{ik} gives the x component of the dipole strength from the state Ψ_i to state Ψ_k. We obtain the y and z component in analogous manner replacing X by Y and Z. $Y = \sum_\nu y_\nu$, $Z = \sum_\nu z_\nu$

Two cases are possible by the determination of c_{ik}.

a.) The functions $\Psi_\mathrm{I}, \Psi_\mathrm{II}, \ldots$ form an orthogonal and normalized system (i. e. $\int \Psi_i \Psi_k d\tau \equiv (\Psi_i \Psi_k) = 0 \quad i \neq k; \quad (\Psi_i \Psi_i) = 1$). In this case we get c_{ik} by forming the scalar product of the equation 7 with Ψ_k

$$(\Psi_k X \Psi_i) = c_{i1} \underbrace{(\Psi_k \Psi_\mathrm{I})}_{=0} + c_{i2} \underbrace{(\Psi_k \Psi_\mathrm{II})}_{=0} + \ldots + c_{ik} \underbrace{(\Psi_k \Psi_k)}_{=1} = c_{ik}$$

$$Q_x = c_{ik} = (\Psi_k, X \Psi_i) \equiv \int \Psi_k X \Psi_i d\tau \tag{8a}$$

b.) The functions are not orthogonal. In order to obtain c_{ik} we must form first the reciprocal system. The members of the reciprocal system $x_\mathrm{I}, x_\mathrm{II}, \ldots$ have the following properties:

$$\int x_i \Psi_k d\tau \equiv (x_i \Psi_k) = 0 \quad i \neq k; (x_i \Psi_i) = 1 \tag{9}$$

Assuming that the x -s are in the same function space as the Ψ-s, or in other words that the x-s are linear combinations of the Ψ-s, $x_i = k_{i1} \Psi_\mathrm{I} + k_{i2} \Psi_\mathrm{II} + \ldots$ we obtain from equ. 9 the following equation system from which the unknown $k_{i1}, k_{i2}, \ldots$ can be determined:

$$\left.\begin{aligned}
(x_i \Psi_\mathrm{I}) &= k_{i1} (\Psi_\mathrm{I} \Psi_\mathrm{I}) + k_{i2} (\Psi_\mathrm{II} \Psi_\mathrm{I}) + \ldots = 0 \\
(x_i \Psi_\mathrm{II}) &= k_{i1} (\Psi_\mathrm{I} \Psi_\mathrm{II}) + k_{i2} (\Psi_\mathrm{II} \Psi_\mathrm{II}) + \ldots = 0 \\
&\ldots \\
(x_i \Psi_i) &= k_{i2} (\Psi_\mathrm{I} \Psi_i) + k_{i2} (\Psi_\mathrm{II} \Psi_i) + \ldots = 1
\end{aligned}\right\} \tag{10}$$

With aid of the reciprocal system we obtain c_{ik} as follows: We form the scalar product of equation 7 with x_k

$$(x_k X \Psi_i) = c_{i1} (x_k \Psi_\mathrm{I}) + c_{i2} (x_k \Psi_\mathrm{II}) + \ldots + c_{ik} (x_k \Psi_k) + \ldots = c_{ik}$$

$$Q_x = c_{ik} = (x_k X \Psi_i) \equiv \int x_k X \Psi_i d\tau \tag{8b}$$

It seems that hitherto only the first formula, 8a, was used, and the second, 8b, overlooked.

2. *Reduction of the $\int x_k X \Psi_i d\tau$ integral to ground integrals.* The x-s are linear combinations of the Ψ-s, (molecular states) The latters are linear combinations of the ψ -s, (canonical structures) Finally the canonical structures are linear combinations of some Slater functions, φ -s. That means that the $\int x_k X \Psi_i d\tau$ integral can be reduced to integrals $\int \varphi_i X \varphi_k d\tau$ involving Slater functions (spin states)

$$\int \varphi_i X \varphi_k d\tau \equiv (\varphi_i X \varphi_k) = \frac{1}{N!} \int \Big(\sum_P (-1)^P P\, a(1) b(2) \ldots \alpha(1) \beta(2) \ldots \Big)$$
$$X \Big(\sum_P (-1)^{P'} P' a(1) b(2) \ldots \beta(1) \alpha(2) \ldots \Big) d\tau$$

It has been proved that this integral can be transformed in the following simplified form: (8)

$$(\varphi_i X \varphi_k) = \int (a(1) b(2) \ldots \alpha(1) \beta(2) \ldots)$$
$$X \Big(\sum (-1)^P P a(1) b(2) \ldots \beta(1) \alpha(2) \ldots \Big) d\tau$$

Taking into account the orthogonality and normalization of the spin variable

$$(\alpha_{(i)}\beta_{(i)})=0 \quad (\alpha_{(i)}\alpha_{(i)})=1 \quad (\beta_{(i)}\beta_{(i)})=1$$

we get the following rules for the integrals:

(We restrict ourselves to the transpositions. The essential is always the order of the spins by φ_i and φ_k)

a.) If there are more than one transpositions between the order of spins by φ_i and φ_k the integral vanishes.

b.) If one transposition is necessary to obtain the same order of spins by φ_i as φ_k, then we get one member from the sum, by which P is just the transposition which reestablishes the same order of spins. $\int a(1)\,b(2)\ldots X\,.\,a(2)\,b(1)\ldots d\tau=(ab)$. We call this term, *exchange integral.*

c.) If $\varphi_i=\varphi_k$, we obtain one term of the following type: $\int a(1)\,b(2)\ldots X\,a(1)\,b(2)\ldots d\tau$ *principal integral* $(abc\ldots)$ and so many exchange integrals as many possibilities we have to permute the electrons having parallel spins.

(E. g. in the case of six electrons:

$$\int a(1)b(2)\ldots X.a(2)b(1)\ldots d\tau=(ab)$$

$$\int a(1)b(2)\ldots Xa(1)b(2)\ldots d\tau=(abcdef)$$

$$\varphi_{\mathrm{I}}=\begin{pmatrix}a&b&c&d&e&f\\ \alpha&\alpha&\alpha&\beta&\beta&\beta\end{pmatrix}\quad \varphi_{\mathrm{II}}=\begin{pmatrix}a&b&c&d&e&f\\ \alpha&\alpha&\beta&\alpha&\beta&\beta\end{pmatrix}\quad \varphi_{\mathrm{III}}=\begin{pmatrix}a&b&c&d&e&f\\ \beta&\beta&\alpha&\beta&\alpha&\alpha\end{pmatrix}\quad \varphi_{\mathrm{IV}}\ldots$$

$$a)\ (\varphi_{\mathrm{I}}\varphi_{\mathrm{III}})=0 \qquad b)\ (\varphi_{\mathrm{I}}\varphi_{\mathrm{II}})=-(cd)$$

$$c)\ (\varphi_{\mathrm{I}}\varphi_{\mathrm{I}})=(abcdef)-(ab)-(ac)-(bc)-(ed)-(df)-(ef)$$
$$(\varphi_{\mathrm{II}}\varphi_{\mathrm{II}})=(abcdef)-(ab)-(ad)-(bd)-(ec)-(cf)-(ef)$$

3. *The principal integral.* We take for example the benzene. The molecule should be in the xy plane, the z axis being perpendicular to the plane of the molecule. The Slater-type form of a π electron function by the a-th C atom is then: (9)

$$a(1)=\left(\frac{\alpha^5}{\pi}\right)^{1/2}z_a e^{-\alpha r_a}=kz_a e^{-\alpha r_a}=kr_a\cos\vartheta_a e^{-\alpha r_a}$$

where ϑ_a, r_a means the spherical coordinates of the electron with respect to the a-th atom.

We take the origin of the coordinate system in the symmetry centre of the benzene molecule. The coordinates of the a-th atom then are: a_x and a_y The coordinates of the electrons are:

x, y with respect to the origin
x_a, y_a with respect to the a-th atom

$$\left.\begin{aligned}x&=a_x+x_a\\ y&=a_y+y_a\end{aligned}\right\}\ (11)\qquad \left.\begin{aligned}x_a&=r_a\sin\vartheta_a\cos\varphi_a\\ y_a&=r_a\sin\vartheta_a\sin\varphi_a\end{aligned}\right\}\quad z_a=r_a\cos\vartheta_a \qquad (12)$$

a.) The x principal integral.

$$\int a(1)b(2)\ldots f(6)\,[x_1+x_2+\ldots+x_6]\,a(1)b(2)\ldots d\tau_1\,d\tau_2\ldots d\tau_6=$$
$$=\int a(1)x_1a(1)d\tau_1\cdot\underbrace{\int b(2)b(2)d\tau_1}_{1}\cdot\underbrace{\int\ldots}_{1}\underbrace{\int f(6)f(6)d\tau_6}_{1}+$$

$$+\int b(2)x_2 b(2)d\tau_2+\int c(3)x_3 c(3)d\tau_3+\ldots+\int f(6)x_6 f(6)d\tau_6$$
$$=J_1+J_2+\ldots+J_6$$
$$J_1=\int a(1)x_1 a(1)d\tau_1=\int a(1)a(1)[\alpha_x+x_a(1)]d\tau_1=a_x\int \underbrace{a(1)a(1)d\tau_1}_{1}+$$
$$+\int a(1)a(1)x_a(1)d\tau_1=a_x+\int \underbrace{k^2z_a^2e^{-2\alpha r_a}}_{a(1)a(1)}\cdot\underbrace{r_a\sin\vartheta_a\cos\varphi_a}_{x_a}\cdot\underbrace{r_a^2\sin\vartheta_a dr_a d\vartheta_a d\varphi_a}_{d\tau(1)}=$$
$$=a_x+k^2\int_0^\infty\int_0^\pi\int_0^{2\pi} r^5e^{-2\alpha r}\cdot\cos^2\vartheta\sin^2\vartheta\cdot\cos\varphi\cdot dr\cdot d\vartheta\cdot d\varphi=$$
$$=a_x+k^2\int_0^\infty\int_0^\pi (r^5e^{-2\alpha r}\cos^2\vartheta\sin^2\vartheta\,dr\,d\vartheta)\underbrace{\int_0^{2\pi}\cos\varphi\,d\varphi}_{=0}=a_x$$

Likewise $J_2=b_x\ldots J_6=f_x$ $J_1+\ldots+J_6=\underline{a_x+b_x+c_x+d_x+e_x+f_x}$ (12a)

b.) The y principal integral. We get in analogous manner

$$\int a(1)\,b(2)\ldots[y_1+y_2+\ldots+y_6]\,a(1)\,b(2)\ldots d\tau=$$
$$=\underline{a_y+b_y+c_y+d_y+e_y+f_y} \qquad (12b)$$

c.) The z principal integral. In the case of plane molecule $z_a=z_1$, and therefore

$$\int a(1)\,b(2)\,[z_1+z_2+\ldots+z_6]\,a(1)\,b(2)\ldots d\tau=$$
$$=\int a(1)z_1\,a(1)\,d\tau_1+\ldots+\int f(6)\,z_6 f(6)\,d\tau_6=J_1+\ldots+J_6$$
$$J_1=\int a(1)\,a(1)\,z_a d\tau_1=\int k^2z_a^3e^{-2\alpha r_a}\,d\tau=$$
$$=\int_0^\infty\int_0^\pi\int_0^{2\pi}\underbrace{k^2r^3\cos^3\vartheta}_{z^3}\cdot e^{-2\alpha r}\cdot\underbrace{r^2\sin\vartheta\,dr\,d\vartheta\,d\varphi}_{d\tau}=$$
$$=\int_0^\infty\int_0^{2\pi}k^2r^5e^{-2\alpha r}\cdot dr\,d\varphi\cdot\underbrace{\int_0^\pi\cos^3\vartheta\sin\vartheta\,d\vartheta}_{=0}=0$$

Likewise $$J_2=\ldots=J_6=0. \qquad (12c)$$

Snmmarizing the results, we have obtained the following formulas in the case of plane molecule for the principal integral:

$$(abcdef)_x=a_x+b_x+c_x+d_x+e_x+f_x;$$
$$(abcdef)_y=a_y+b_y+c_y+d_y+e_y+f_y\quad(abcdef)_z=0.$$

4. *The exchange integral.* Let us consider for example the following exchange integral:

$$(ab)_x=\int a(1)\,b(2)\,c(3)\ldots[x_1+x_2+\ldots+x_6]\,a(2)\,b(1)\,c(3)\ldots d\tau$$

$$(ab)_x = \int \underbrace{a(1)x_1 b(1)d\tau_1}_{J_1} . \int \underbrace{a(2)b(2)d\tau_2}_{J_0} . \int \underbrace{c(3)c(3)d\tau_3}_{1} \ldots \int \underbrace{f(6)f(6)d\tau_6}_{1} +$$

$$+ \int \underbrace{a(1)\,b(1)\,d\tau_1}_{J_0} . \int \underbrace{a(2)\,x_2 b(2)\,d\tau_2}_{J_1} . \int \underbrace{c(3)\,c(3)\,d\tau_3}_{1} \ldots \int \underbrace{f(6)f(6)\,d\tau_6}_{1} +$$

$$+ \int \underbrace{a(1)\,b(1)\,d\tau_1}_{J_0} . \int \underbrace{a(2)\,b(2)\,d\tau_2}_{J_0} . \int \underbrace{c(3)\,x_3 c(3)\,d\tau_3}_{c_x} \ldots \int \underbrace{f(6)f(6)\,d\tau_6}_{1} + \ldots +$$

$$+ \int \underbrace{a(1)\,b(1)\,d\tau_1}_{J_0} . \int \underbrace{a(2)\,b(2)\,d\tau_2}_{J_0} . \int \underbrace{c(3)\,c(3)\,d\tau_3}_{1} \ldots \int \underbrace{f(6)\,x_6 f(6)\,d\tau_6}_{f_x} =$$

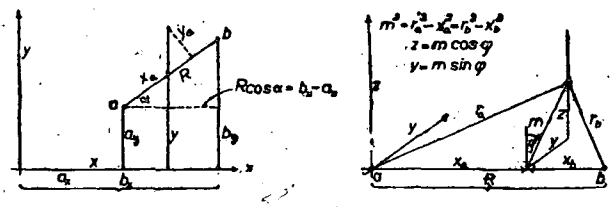
$$= 2J_0J_1 + J_0^2(c_x + d_x + e_x + f_x)$$

$$J_0 = \int a(1)\,b(1)\,d\tau_1 = \int a(2)\,b(2)\,d\tau_2 = \int kz_a e^{-\alpha r_a} . kz_b e^{-\alpha r_b} d\tau = \int k^2 z_a^2 e^{-\alpha(r_a+r_b)} d\tau$$

$$J_1 = \int a(1)\,x_1 b(1)\,d\tau_1 = \int a(2)\,x_2 b(2)\,d\tau_2 = \int k^2 z^2 e^{-\alpha(r_a+r_b)} . x . d\tau$$

$$x = a_x + x_a \cos\alpha - y_a \sin\alpha \qquad (13)$$

In order to evaluate J_0 and J_1 we use the transformation formula 13 and on the other hand we introduce elliptical coordinates $\frac{r_a+r_b}{R} = \mu$ $\frac{r_a-r_b}{R} = \nu$ by means of which the integrals transform as follows:



$$x_a = \frac{R}{2}(1+\mu\nu) \quad x_b = \frac{R}{2}(1-\mu\nu) \quad z_a = z_b = z = \frac{R}{2}\sqrt{(\mu^2-1)(1-\nu^2)}\cos\varphi$$

$$y_a = y_b = y = \frac{R}{2}\sqrt{(\mu^2-1)(1-\nu^2)}\sin\varphi; \quad \iiint F d\tau = \frac{R^3}{8}\int_1^{\infty} d\mu \int_{-1}^{+1} d\nu \int_0^{2\pi} d\varphi (\mu^2-\nu^2) F$$

$$J_0 = \int_1^{\infty}\int_{-1}^{+1}\int_0^{2\pi} \frac{R^3}{8}(\mu^2-\nu^2)\, k^2 \underbrace{\frac{R^2}{4}(\mu^2-1)(1-\nu^2)}_{z^2} \cos^2\varphi\, e^{-\alpha R\mu} d\mu\, d\nu\, d\varphi =$$

$$= \frac{e^{-\beta}}{5}\left(\frac{\beta^3}{3} + 2\beta^2 + 5\beta + 5\right) \quad \beta = \alpha R.$$

The value of R in aromatic molecules is 1.04 A, the value of α in the case of C atom is: 3.25. Substituting these values we get the following value for J_0 (in atomic units) $J_0 = 0.25995$ (10) $J_0^2 = 0.06757$ (square of atomic unit).

$$J_1 = \int_1^{\infty}\int_{-1}^{+1}\int_0^{2\pi} \frac{R^3}{8}(\mu^2-\nu^2).\underbrace{k^2\frac{R^2}{4}(\mu^2-1)(1-\nu^2)}_{z^2}.\cos^2\varphi\,[\underbrace{a_x+x_a\cos\alpha-y_a\sin\alpha}_{x}].e^{-\alpha R\mu}d\mu\,d\nu\,d\varphi =$$

$$= a_x J_0 + \cos\alpha \underbrace{\int_1^{\infty}\int_{-1}^{+1}\int_0^{2\pi} \frac{R^3}{8}(\mu^2-\nu^2).\underbrace{k^2\frac{R^2}{4}(\mu^2-1)(1-\nu^2)}_{z^2}\cos^2\varphi\,\underbrace{\frac{R}{2}(1+\mu\nu)}_{x_a}.e^{-\alpha R\mu}\,d\mu\,d\nu\,d\varphi}_{J_2} -$$

$$- \sin\alpha \underbrace{\int_1^{\infty}\int_{-1}^{+1}\int_0^{2\pi} \frac{R^3}{8}(\mu^2-\nu^2).k^2\frac{R^2}{4}(\mu^2-1)(1-\nu^2).\cos^2\varphi\,\frac{R}{2}\sqrt{(\mu^2-1)(1-\nu^2)}\sin\varphi.e^{-\alpha R\mu}d\mu.d\nu.d\varphi}_{J_3}$$

$$J_2 = \frac{R}{2}J_0 + \underbrace{\int_1^{\infty}\int_{-1}^{+1}\int_0^{2\pi} \frac{R^3}{8}(\mu^2-\nu^2).\underbrace{k^2\frac{R^2}{4}(\mu^2-1)(1-\nu^2)}_{z^2}\cos^2\varphi\,.\frac{R}{2}\mu\nu.e^{-\alpha R\mu}\,d\mu\,d\nu\,d\varphi}_{=0}$$

$$J_3 = \int_1^{\infty}\int_{-1}^{+1} \frac{R^3}{8}(\mu^2-\nu^2).k^2\frac{R^2}{4}(\mu^2-1)(1-\nu^2).\frac{R}{2}\sqrt{(\mu^2-1)(1-\nu^2)}.e^{-\alpha R\mu}d\mu\,d\nu.\underbrace{\int_0^{2\pi}\cos^2\varphi\,\sin\varphi\,d\varphi}_{=0} = 0$$

$$J_1 = a_x J_0 + \cos\alpha.\frac{R}{2}J_0 = J_0\left(a_x+\frac{R\cos\alpha}{2}\right) = J_0\left(a_x+\frac{b_x-a_x}{2}\right) = \frac{J_0}{2}(a_x+b_x).$$

$$(ab)_x = 2J_0J_1 + J_0^2(c_x+d_x+e_x+f_x) =$$
$$= \underline{J_0^2(a_x+b_x+c_x+d_x+e_x+f_x)} \qquad (14a)$$

We get in analogous manner

$$(ab)_y = \underline{J_0^2(a_y+b_y+c_y+d_y+e_y+f_y)} \qquad (14b)$$

It can be proved that all exchange integral between adjacent atoms are of this form.

$(ab)_z = 0$, in the case of plane molecule, as in the case of principal integral. 14c

It is obvious that by benzene, anthracene, naphtaline, the above mentioned sums (12 *a b c*, 14 *a b c*) are equal to zero because of the symmetry of the molecule.

III. *Conclusions. The comparison with the experiment.*

We have reduced the dipole strength integral to two ground integrals: the principal integral and the exchange integral. We have evaluated the latters with aid of Slater-type eigenfunctions.

Our formulae show that in the case of a plane symmetrical molecule these ground integrals are zero and therefore the dipole stength which itself is a linear combination of them, is also zero. That means that the transition is forbidden.

A closer inspection of the formulae shows that there is a possibility of the transition when the sum differs from zero due to the deformation vibrations.

In this step our result is in good agreement with the experimental data. The first band of the benzene is very weak and has a vibrational structure and it is proved (11) that this transition is a

forbidden one. This is shown by the very little oscillator strength value $f = 0{\cdot}0006$.

Our result differs from the experiment concerning the second band of the benzene which has a great oscillator strength. The same is the case by the naphtaline and anthracene. The deviations (and great deviations from the theoretical 0 osc. strength) show the lack of the Slater-Pauling method.

All the molecular states with which this method calculates are purely homopolar states. The ionic, polar states by which two electrons can be by the same atom, are excluded from this treatment.

The result obtained shows that there is no possibility of transition to these homopolar states. We interprete therefore the observed intensity as a transition to a molecular state which is a combination of the homopolar and ionic states.

In this step our result agrees with that of Sklar (12) with the difference that his considerations were only on group therotetical base while we evaluated the integrals, the value of which was easily determined on ground of the molecular structure (the spatial arrangement of the atoms).

Our result agrees with that of Mulliken's who starting from a different point of view found that the transitions of great intensity are always transitions to partly ionic states.

In the next paper we shall use this method by some asymmetrical molecules.

Summary.

We have treated the computation of transition probability on the base of the Slater-Pauling method by some organic symmetrical molecules (benzene, and so on).

The evaluation was reduced to some ground integrals and from these it was to observe that there is no transition between the pure homopolar states with which this method only deals.

The comparison with the experiment shows that the observed transition must be to a partly ionic state in agreement with Mulliken's result.

I wish to express my sincere thanks to Prof. K. Széll for his helpful suggestions and to Prof. B. N. Szőkefalvy for the friendly discussion of the orthogonality problem.

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The Mesomerism of Propenylbenzene and of Allylbenzene Derivatives.

By Á. Kiss, G. Fodor and J. Molnár.

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Introduction.

In continuation of a previous investigation (1) it deemed of interest to study differences between the intensity of the inductive and of the mesomeric resp. electromeric effect by measuring the ultraviolet absorption curves of several derivatives of benzene with a propenyl resp. allyl sidechain. Absorption data of the following compounds are reported here and will be discussed in detail: allylbenzene, propenylbenzene, phenol, anisol, guaiacol, veratrole, anol, anethol, eugenol, isoeugenol, chavibetol, isochavibetol, safrol, isosafrol, homogenol, isohomogenol, myristicin, isomyristicin.

Discussion.

The extinction curve of allylbenzene (curve 2) is similar to that of benzene (curve 1) but influenced by the inductive effect of the allyl group. The π-electrons of the olefinic linkage are isolatad from those of the benzene nucleus by a methylene group, consequently they can not participate in the mesomerism of benzene (cf. Ia). They increase only the extinction values of benzene in the ascending branch blurring thereby near to 220 mμ the curve. The curve of benzene is highly infuenced by the mesomerism of the adjacent double bond of the propenyl chain e. g. in the case of propenylbenzene (curve 3). Resonating forms (IIa—IIb) result in decreasing the energy for excitation, therefore the extinction curve is shifted in comparison to that of allylbenzene (curve 2) towards the visible. On the other hand, participation of polar mesomeric forms (IIa—IIb) even in the ground state causes an increase of excitation. Excitation is therefore connected with a shift of charge.

The curve of phenol (curve 4) shows a benzene spectrum (2) altered mesomerically by the hydroxyl group (IIIa—IIIb). These mesomeric forms are less probable, owing to the electronic affinity of the oxigen atom.

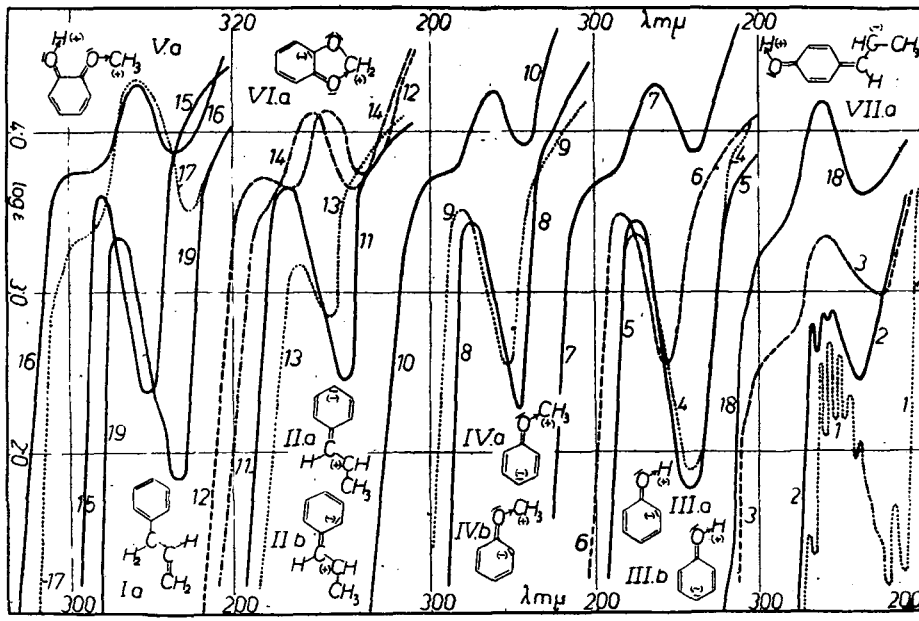
The close resemblance of the curves of phenol (curve 4) and of anisol (curve 19) proves, that etherification of a phenolic hydroxyl group does not affect the probability of mesomerism (IVa—IVb). Similarly, the curve of guaiacol (curve 5) agrees with that of phenol (curve 4), they occur consequently in related mesomeric forms. A mesomeric tendency of both groups, as by Va, seems to be improbable. This consideration is further supported by the resemblance of the curve for guaiacol (curve 5), to that for veratrol (curve 8), indicating that etherification of the second hydroxyl group is without influence upon the mesomeric system of the compound.

The curve of 1,2-methylenedioxybenzene reveals a resemblance (cf. VIa) to that of guaiacol (cf. Va) and veratrol, resp. Differences

can be explained by the strain caused by the five membered hetero-ring. The mesomerism of this compound was altered by entrance of a methoxy group in o-position, as given by 1,2-methylenedioxy--3-methoxybenzene.

These experimental facts lead to the conclusion that the extinction curves of the treated phenol derivatives are inductively or electromerically influenced benzene spectra. Only slight influence is exerted by the substitutents, indicated by the percentual increase of the region limited by the extinction curves, in comparison to that of phenol.

Summarised, we can say that the curves of allyl benzene derivatives correspond closely to those of the appropriate phenols resp. phenol ethers: allylbenzene (curve 2) to benzene (curve 1), eugenol (curve 6) and chavibetol (curve 15) to guaiacol (curve 5), homogenol



(curve 9) to veratrol (curve 8), safrol (curve 11) to 1,2-methylenedioxybenzene, myristicin (curve 13) to 1,2-methylenedioxy-3--methoxy-benzene. Slight differences are only due to the inductive effect of the allyl chain, estimated by the percentual increase of extinction. The own extinction of the allyl chain could only be observed in the ascending part of the curves.

The absorption spectra of all propenyl derivatives: *p*-anol (curve 17), anethole (curve 18), isoeugenol (curve 7), isohomogenol (curve 10), isosafrol (curve 12), isomyristicin (curve 14), isochavibetol (curve 16) reveal a close resemblance to that of propenylbenzene (curve 3). This fact indicates that π-electrons of the propenyl chain play an important part in the mesomerism of propenyl benzene derivatives (cf. VIIa). Differences between the extinction curves of the single propenylbenzene derivatives can be explained as well by their own mesomerism as by the inductive effect of the

substituents. This effect could be estimated quantitatively on comparing the percentual increase of extinction values with those of propenyl benzene.

Summary.

The ultraviolet absorption curves of a number of allyl and propenyl phenols and their ethers were investigated. The mesomeric effect of the substituents was in all cases apparently larger than their inductive effect.

A uniform explanation of these effects could be given by the critical examination of all possible mesomeric forms in the ground state and in the excited state. The allyl resp. propenyl groups have only a small inductive resp. a strong mesomeric effect upon the extinction curve of benzene. The difference due to this effect is to be found in case of all the investigated derivatives of allyl benzene resp. propenyl benzene.

Experimental.

The measurements of absorption spectra were carried out by Molnár (4) The method and apparatus used was the same as reported previously (5). Purification and control of the compounds was carried out according to the procedures recorded in a recent communication (1).

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Zur Lichtabsorption der N-[Aryl-thio-alkyl]-phtalimid-Derivate.

Von Á. Kiss, E. Vinkler und E. Csetneky.

(Eingegangen am 2. März. 1949.)

Einleitung.

Da nach den, uns zur Verfügung stehenden Literaturdaten die Lichtabsorption der N-(Aryl-thio-alkyl)-phtalimid-Derivate nicht bekannt ist, so wurde die Erforschung dieser Frage in Begriff genommen. Damit bezweckten wir auch diese Anomalien, welche in den physikalischen, bzw. chemischen Eigenschaften (Schmelzpunkte Verbrennungswärmen, Polymorphysmus, bzw. Alkaliempfindlichkeit (1) dieser Verbindungen sich zeigen, zu beantworten. Das optische Verhalten der Phenolderivate ist wohl, diese der isologen Sulfide weniger bekannt. Im Besitze der Extinktionskurven der Schwefelderivate können die Unterschiede der Wirkungen induktiver und mesomerer Art der O-, bzw. S-Atome aufgeklärt werden.

Die untersuchten, teils neuen Verbindungen, haben Vinkler und Szabó (2) hergestellt. Die Extinktionskurven der p. a. reinen Präparate hat Csetneky in spektroskopisch reinem Aethanol (3) bei Zimmertemperatur ausgemessen. Die Experimentelle Einrichtung und die Messmethode betreffend werweisen wir auf früheren Arbeiten (4).

Besprechung der Versuchsdaten.

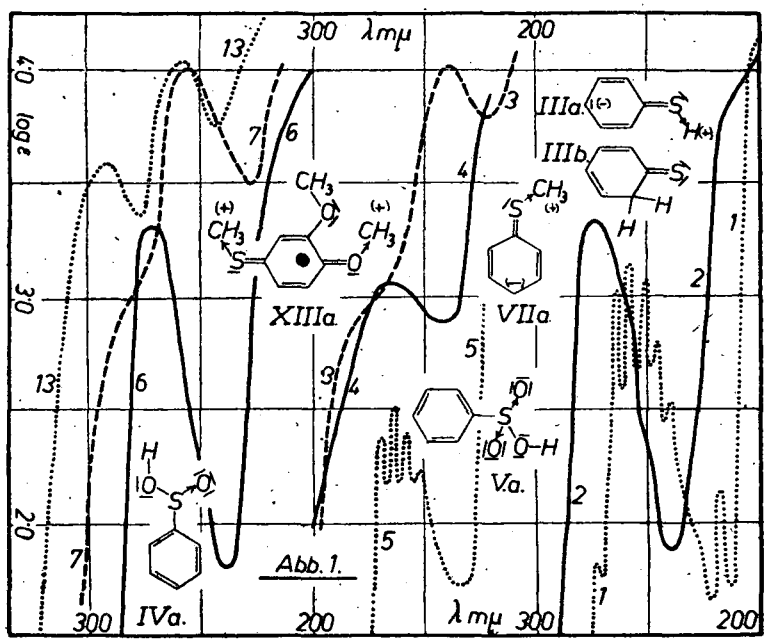
Wie früher gezeigt wurde (5) gestattet die Abschätzung der möglichen elektromeren Grenzstrukturen des Grund- und Anregungszustandes die Erklärung der Struktur der Extinktionskurven. Somit versuchen wir diese Frage auch bei den untersuchten Verbindungen gleicher Weise zu beantworten. Um Wiederholungen zu vermeiden, verweisen wir auf eine frühere Arbeit (6). Um Raum zu sparen werden nur die wichtigsten mesomeren Grenzformen wiedergegeben.

Die Kurven des Benzols (I) und des Phenols (II) (Abb. 1, Kurven 1 und 2, nachher: 1/1 und 1/2) wurden früher (6) eingehend besprochen.

Die Mesomerie des Thiophenols (III) ist dieser des Phenols (6) ähnich. Wegen der schwächeren Elektronenaffinität des S-Atoms werden aber, die mit π-Elektronenabgabe entstehenden mesomeren Grenzformen IIIa—IIIb (Abb. 1) im Grundzustand von III eine grössere Rolle spielen, als bei Phenol (6). Somit ist die Kurve (1/3) von III (7) ein, in grösserem Masse verändertes Benzolspektrum (1/1) als diese des Phenols (1/2). U. E. kann die stark abweichende Struktur der Kurven (1/2 und 1/3) beider Verbindungen derweise erklärt werden, dass bei Thiophenol die Anregung der einsamen Elektronenpaare des S-Atoms eine Rolle spielt. Die verwischte Bande von III in der Gegend von 270 mμ sollte der Phenolbande

(274 mμ) entsprechen. Die Phenolbande entspricht ihrerseits der deformierten und mit zunehmender Intensität nach den langen Wellen verschobenen Hauptbande des Benzols (255 mμ). Dafür spricht der experimentelle Befund, das in Heptan (8) und in konzentrierterer Säurelösung (9) die Phenolbande Schwingungsstruktur aufweist. Die bei 258 mμ liegende hohe Bande von III bedingt die Anregung der einsamen Elektronenpaare des S-Atoms. Die Richtigkeit dieser Annahme unterstützt der experimentelle Befund (7), dass bei Benzolsulfinsäure (IV) und bei Benzolsulfosäure (V) (6), wo die einsamen Elektronenpaare des S-Atoms teilweise, bzw. vollständig in Anspruch genommen wurden diese Bande (1/4) fehlt, bzw. man erhält (10) das, durch die induktive Wirkung beeinflusste Benzolspektrum (1/5).

Der beinahe gleiche Verlauf der Kurven von Phenol und Anisol (VI) (1/2 und 1/6) weist darauf hin, dass durch die Aetherifizierung die Mesomerie des O-Atoms kaum geändert wird (11). Demgegenüber wird die ganze Extinktionskurve (1/7) des Thioanisols (VII) besonders dessen hohe Bande zu dieser des Thiophenols (1/3) nach den langen Wellen verschoben. Dabei nimmt auch die Extinktion zu. Im allgemeinen übt die Aetherifizierung der HO-Gruppe eine Extinktionsabnahme aus (11, 12). Das entgegengesetzte Verhalten des Thioanisols kann nicht in befriedigender Weise erklärt werden. Sonst sind die Kurven von Thiophenol (1/3) und Thioanisol (1/7) ähnlich strukturiert, wodurch das bei Thiophenol Gesagte bestätigt wird.



Wegen der grössten Anzahl von Doppelbindungen beherrscht die Grenzform VIIIa (Abb. 2) den Grundzustand des Phtalimids (VIII). Wegen der kleineren Anzahl von Doppelbindungen werden

die Grenzformen VIIIb—VIIId erst in dem angeregten Zustand eine Rolle spielen. Die Erste Bande bei 295 mμ bedingt die Anregung der zwei Carboxylgruppen (2/8). Die Entstehung der bei 236 mμ liegenden scharfen Bande ist schwer zu erklären.

Die Mesomerie des N-Methylphtalimids (IX) ist zu dieser der vorigen Verbindung ähnlich, worauf die gleiche Struktur der Kurven beider Verbindungen hinweist (2/8 und 2/9). Die Extinktonsabnahme der ersten bande von IX kann nicht befriedigender Weise erklärt werden.

Nach Literaturangaben (13) sollte die Extinktion des N-(Phenyl-thio-methyl) phtalimids (X) wegen der isolierenden Wirkung der H_2C-Gruppe aus der Eigenabsorption des Methylphtalimids und des Thiophenols, bzw. aus dieser des Phtalimids und des Thioanisols sich zusammensetzen. Die grossen Unterschiede der experimentell erhaltenen und erwehnter Weise berechneten Kurven zeigen, das die erwähnte Additivität der Extinktionen überhaupt nicht besteht. Dies ist wegen der grossen Unterschiede der Kurven von Thiophenol (1/3) und Thioanisol (1/7), weiterhin von Phtalimid (2/8) und von N-Methylphtalimid (2/9) verständlich. Dem zu Folge erwartet man, dass Phenyl-alkyl-sulfide und N-Alkyl-phtalimide in ihren Extinktionskurven Unterschiede aufweisen werden. Dies zu klären sind Untersuchungen im Gange.

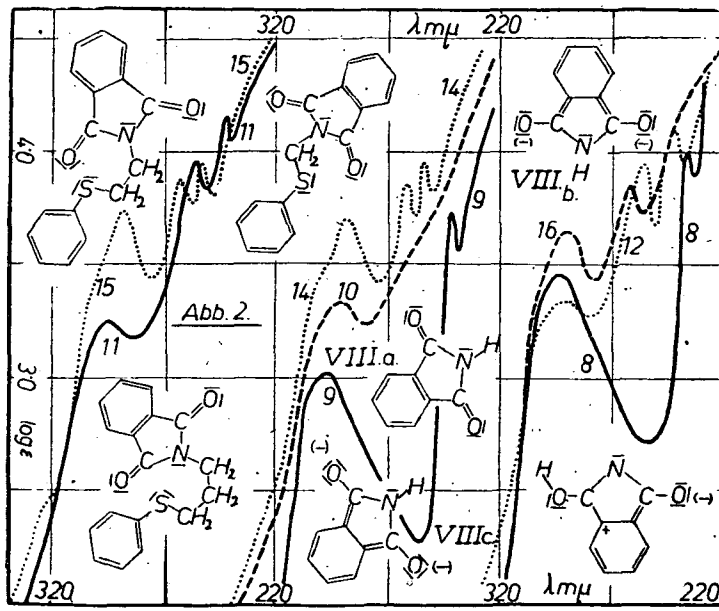
Bei N-[β-(phenyl-thio)-aethyl]-phtalimid (XI) und bei N-[γ-(phenyl-thio)-propyl]-phtalimid (XII) treten, wahrscheinlich wegen der stärkeren isolierenden Wirkung der Aethylen- und Propylen-Gruppen, die charakteristischen Banden des Thioanisols (1/7) und Phtalimids (2/8), welche bei dem Methylen-Derivat noch verwischt sind scharf auf (2/11 und 2/12, bzw. 2/10). Die Aethylen- und Propylen-Derivate können in mehreren stereoisomeren Formen vorkommen (Vgl. Abb. 2, XIa und XIIa). Von diesen können einige aus sterischen Gründen gehindert, andere wegen Wechselwirkung der Nachbaratome: S und O, bzw. N und S (Abb. 2, XIa und XIIa) bevorzugt sein.

Die grösseren Extinktionsunterschiede der Kurven von 3,4-Dimethoxy-thioanisol (XIII) und Thioanisol (2/13 und 2/7) können derweise erklärt werden, dass das O-Atom der p-stelligen Methoxygruppe zieht das S-Atom in die Mesomerie des Benzolringes herein (Abb. 2, XIIIa). Somit wird der Grundzustand von XIII durch die Grenzform XIIIa beherrscht. Diese Wirkung äussert sich in der Extinktionszunahme der ersten Bande (296 mμ). Die zweite bande bei 258 mμ entspricht sogar der Lage nach der Bande des Thioanisols (1/7), bzw. des Thiophenols (1/3). Dadurch wird unsere Annahme, dass diese durch die Anregung der π-Elektronen des S-Atoms bedingt wird, nochmals bestätigt.

Bei der Kurve (2/14) des N-[(3,4-Dimethoxy-phenyl-thio)-methyl]-phtalimid (XIV) kann von der Additivität der Extinktionen von 3,4-Dimethoxy-thioanisol und Phtalimid noch weniger die Rede sein, als bei der vorerwehnten Verbindungsreihe. Das Gleiche trifft die Extinktionen der Derivate N-[β-(3,4-Dimethoxy-phenyl-thio)-eathyl]-phtalimid (XV) und N-[γ-(3,4-Dimethoxy-phenyl-thio)-propyl]-phtalimid (XVI) (2/15 und 2/16).

Auffallend sind die Strukturunterschiede der entsprechenden Phenyl-, bzw. 3,4-Dimethoxyphenyl-Derivate (2/10, 2/11 und 2/12,

bzw. 2/14, 2/15 und 2/16). Bei der ersterwehnten Verbindungsreihe verschwindet die Bandenstruktur bei dem Methyl-Derivat (2/10), was im Sinne des oben Gesagten zu erklären ist Bei der zweiten Reihe kommt bei allen drei Derivaten eine gleiche Anzahl von Banden vor (2/14, 2/15 und 2/16). Dieses anomale Verhalten der Kurven kann erst im Besitze eines grösseren Versuchsmaterials aufgeklärt werden. Es steht in Zusammenhang mit der Anomalie der physikalischen und chemischen Eigenschaften dieser Verbindungsreihe (1, 2).



Zusammenfassung.

Es wurden die Extinktionskurven von sechs N-[Aryl-thio-alkyl]-phtalimid-Derivaten, weiterhin diese des Thioanisols, 3, 4-Dimethoxy-thioanisols, Phtalimids N-Methyl-phtalimids neu ausgemessen.

Bei den N-[Aryl-thio-alkyl]-phtalimid-Derivaten kann, trotz der isolierenden Wirkung von gesättigten Kohlenwasserstoffketten die Additivität der Extinktionen der Chromophore (N-Methylphtalimid und Thioanisol, bzw. 3,4-Dimethoxythioanisol) nicht in Frage kommen.

Bei den einzelnen Gliedern beider homologen Reihen ändert sich die Struktur der Extinktionskurven verschiedener Weise mit der Anzahl der C-Atome der Kohlenwasserstoffkette.

Um die, in den Extinktion der untersuchten Derivate gefundenen Anomalien aufzuklären sind weitere Versuche im Gange.

Szeged (Ungarn) Februar 1949.

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Contribution from the Experimental Physical Institute of the University of Szeged.
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About the Inner Photoelectric Effect of Gelatineous Dyestuffs.

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Introduction.

According to B. Gudden and R. W. Pohl a splitting of electrons comes into existence in every substance illuminated by a light of suitable wavelength under suitable circumstances (1). If these split electrons are conducted by an outer electric field in the same substance in which they were split from the atom, then we call this phenomenon an inner photoelectric effect. The current caused by the moving of split electrons is called photoelectric negative primary current. On account of the moving of molecules caused by heat, the positive rest of the atom takes over an electron from one of its neighbour situated nearer to the cathode, in consequence of this, the neighbour will be positive. Thus it may well be that the ion itself does not wander, only the position of the negative charge gets nearer to cathode, this causes a current called positive primary current by B. Gudden and R. W. Pohl (2).

In an ideal case when the substitute of split electrons is so fast that the shifting of charge does not cause any permanent change in the substance, the primary current is constant. The primary current is without inertia and proportional to the absorbed energy, and to field strength if the field strength is not high. If the field strength is high the primary current approaches a maximum (3).

In most cases the speed of substitute of electrons — the strength of positive primary current — depends on the quality of material, temperature and illumination. The substitute of electrons goes so slowly, that after the first splitting of electrons the inner photoelectric effect occurs in a new material from the point of view of photoelectric effect. Consequently, the strength of positive primary current is not constant in time. In addition, other phenomena may occur which cause a secundary current (e. g. electrolytic conduction, rise of space charge etc).

In case of semiconductors the circumstances are most complicated. These have a little conductivity also in darkness: the current is called dark current. Here the negative primary, positive primary, secundary and dark currents are flowing simultaneously under illumination. The difference between currents measured in light and in darkness (shortly, photocurrent) cannot be considered as a photoelectric current. Only one thing is sure i. e. that it is of photoelectric origin. The observed change of conductivity may form an important part of koherer effect, which may be concluded from the fact that the change of conductivity depends on its former condition and in some cases (e. g. selenium) on mechanical shuttering. In these cases the secundary current may be a multiple of the original photoelectric current.

If we want to investigate the pure photoelectric primary current we have to quicken the substitute of split electrons as much as possible and we have to hinder the rise of greater secondary currents. This may be attained by using little thickness and by choosing as little intensity as possible and as short a time of illumination as possible. Further we return the substance to its original condition after every measurement (by simple waiting, or heating or by red illumination).

Experimental.

The investigation of outer photoelectric phenomena show that the shorter the wavelength the more intensive is the splitting of electrons. (4). Therefore I used a spark as a source of light, the electrodes of which were aluminium plates. The light of the spark was focussed on the phosphor by means of one lense.

The substance of phosphor was rhodulin orenge N (5). The absorbing area of the plate was 1×3 mms and its thickness was 0,1 mm. The directions of illuminating light and of the electric field during the experiment were perpendicular. The experimental equipment is sketched in Fig. 1.

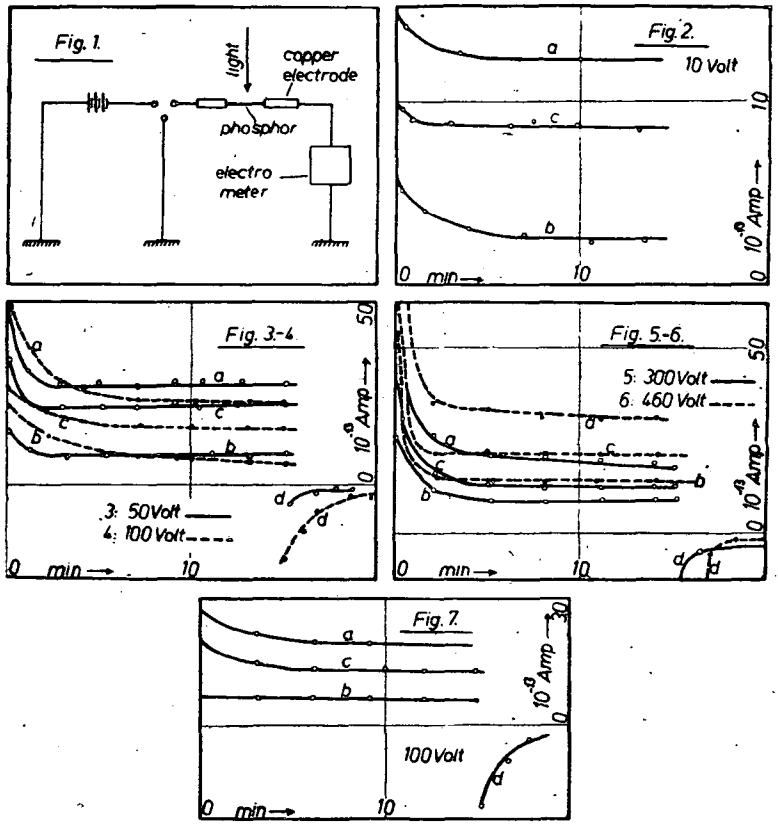
A common dyestuff plate does not show any measurable inner photoelectric effect. If the plate is heated before measuring then a measurable photoelectric current is obtainable. The heating was carried out in an electric furnace. I raised the temperature of the plate to a degree of 150° C at a rate of 3° C/min, and I kept it at this degree for 3 hours. It is not allowed to put the dyestuff plate immediately into a space of a temperature of 150° C on account of the alteration of plate (6).

I used a Lindemann electrometer for measuring the current. I calculated the intensity of current from the capacity and speed

of the charging of electrometer in the usual manner. The little capacity and great sensitiveness of the electrometer made an exact measurement of very small intensities (10^{-14} Amp.) possible

The changing of sensitiveness of electrometer enabled us to have a short measuring time (a few seconds) in every experiment. In this way the results were not influenced by secondary currents. Secondly I have to return the phosphor to its original condition after each measurement. This was carried out simply by resting the phosphor for 5 minutes in darkness without an electric field.

The photocurrent was calculated from the results of two measurements carried out immediately one after the other. I measured



the intensity of current first during irradiation and immediately afterwards in darkness. The difference between the results of these measurements was the photocurrent.

Results.

A) Photocurrent Under Use of a Constant Outer Voltage.

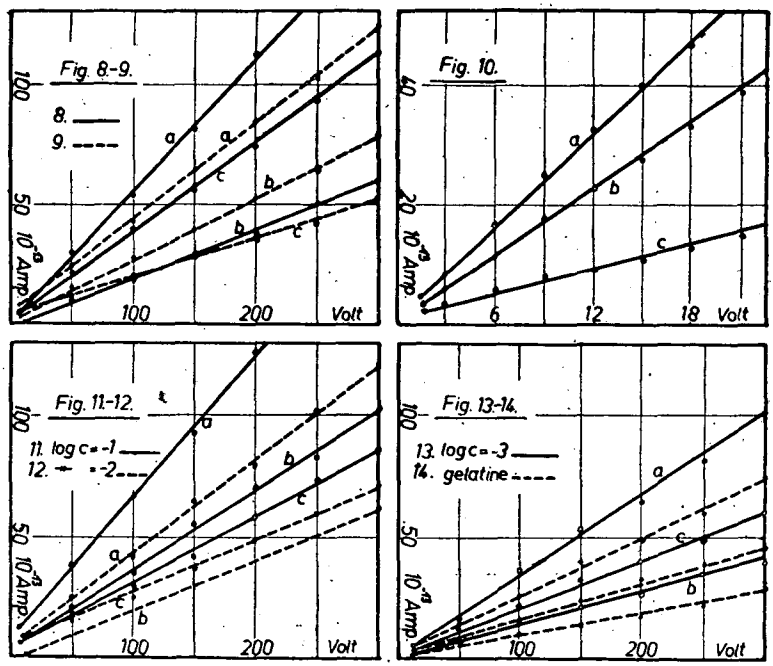
If the phosphor is kept under constant potential and is permanently irradiated by light, then we receive the current curves shown in Fig-s 2, 3, 4, 5, 6. The abscissa represents time, while the ordinate represents intesity of current flowing through the phosphor. Each figure shows current curves belonging to 10, 50, 100, 300

and 460 V-s outer voltages respectively. The curve *(a)* represents the intensity measured under illumination while the curve *(b)* represents that dark current. The third curce *(c)* represents the photocurrent. If the outer voltage is switched off we receive a current flowing in the opposite direction called secondary current. (Curve *d*).

The more important rules drawn from the results are as follows:

1. Each kind of current decreases in time and only after a certain time takes a constant value.

2. In cases of greater voltage the values of photo- and dark currents, at the beginning, not only decreases at a high rate from the absolute value to a constant value, but the decrease is more abrupt. (Table I. 2. and 3. line).



3. The photocurrent is a smaller percentage of dark current, at the beginning value, than under the same outer voltage at the constant value (The last line of Table I).

4. The photocurrent is a greater percentage of dark current when the outer voltage is smaller, although the absolute value of photocurrent is increasing when the outer voltage is increased (The last line of Table I).

5. The value of secondary current, at the beginning, is greater when the outer voltage is greater. Similarly the steepness of curves belonging to secondary current also increases when the outer voltage is increased (*d* curve on Fig-s 2, 3, 4, 5, 6).

It is well known that the intensity of current flowing in gelatineous dyestuffs under outer voltage, is diminishing for a short time, then becomes constant (7).

Table I.

	Outer Voltage Volt-s	Dark current	Photocurrent	Percentage, calculated from dark current and photocurrent
		Unit: 10^{-13} Amp		
Beginning value	10	5,2	10	192
Constant value		3,4	9,2	270
Difference between beginning and const. value		1,8	0,8	—
Percentage calculated from beginning and constant value		35	8	—
Beginning value	50	11	15	136
Constant value		5	13	260
Difference		6	2	—
Percentage		55	13	—
Beginning value	100	20	27	135
Constant value		6	10	167
Difference		14	17	—
Percentage		70	63	—
Beginning value	300	35	45	129
Constant value		8	11	137
Difference		27	34	—
Percentage		77	66	—
Beginning value	460	55	65	118
Constant value		14	17	121
Difference		41	48	—
Percentage		75	74	—

Fig. 7. shows the inner photoelectric effect of a gelatineous dyestuff plate formerly kept under 100 V outer voltage for 15 min-s, consequently its resistance was constant from the point of view of dark current. Yet it is to be seen that its resistance from the point of view of photoelectric current is not constant in time, although, compared with the correspondent Fig. 4. we see that the difference between beginning and constant value is not so great, further that the constant value is reached sooner. The constant value of photocurrent is the same in both cases.

B) The Photocurrent as the Function of Outer Voltage.

If the value of photocurrent as the function of outer voltage is investigated, we receive the curves shown in Fig-s 8, 9, 10. As is to be seen the intensity of photocurrent increases linearly with the increasing of outer voltage, i. e. Ohm's law is valid not only for dark current but also for photocurrent.

Table II.

Outer voltage		10	50	100	150	200	250	300
Dark current	unit:	not measurable	3	7	11	15	20	24,2
Photocurrent	10^{-13} A	12	8	15,6	22	29,8	37,6	45
Percentage		267	223	200	198	188	186	

Table III.

Outer voltage		10	50	100	150	200	250	300
Dark current	unit:	1,5	13	24	40	53	63	78
Photocurrent	10^{-13} A	4	10	18	29	36	42	51
Percentage		266	77	75	72,5	68	66,5	65,5

Table IV.

Outer voltage		1,5	3	6	9	12	15	18	21
Dark current	unit:	3	6	11	17,4	22,8	26	34	39
Photocurrent	10^{-13} A	1,6	3	5,6	7,8	9,8	11	14	15,6
Percentage		53,5	50	47,2	45	43,5	42,5	41	40

The photoeffect measured immediately after heating is shown in Fig. 8. There is no measurable dark current under small voltage (about 20 V), only the photocurrent is measurable. The value of photocurrent is always greater than that of dark current, but the percentage is decreasing when outer voltage is increased (Table II).

Fig. 9. shows the same current as Fig. 8. excepting that the gelatineous dystuff plate was kept for one day, after heating, in open air until the measurements were carried out. Comparing the results with those received immediately after heating, we see that the percentage is smaller in the case of plates kept for one day in open air (Table III.).

If we keep the plate in open air for two weeks after heating and afterwards measure the photoeffect, we receive the results shown in Fig. 10. On account of the great conductivity we can use only small voltage because the dark current would be too great if we used great voltage. In this case the photocurrent is always smaller than the dark current and the percentage is also smaller than in the two former cases (Table IV.).

C) Photocurrent as the Function of Concentration.

The inner photoelectric effect of gelatineous dyestuff plates having concentrations of —1,0 —2,0, —3,0 and that of pure gelatine plate is shown in Fig-s 11, 12, 13, 14. The greatest photocurrent flows through the plate of greatest concentration under every voltage. The percentage shows that the absolute value of photocurrent, in cases of plates of greater conductivity, is greater, yet, the photocurrent is a smaller percentage of dark current than in cases of smaller conductivity (Table V.).

Conclusions.

The photocurrent cannot be considered as a pure photoelectric primary current. We can only say that it is of photoelectric origin. In this way we can explain the dependence of photocurrent on the former condition of plate (Comparing the 4. and 7. experiments). Many kinds of currents slow simultaneously on account of using a source of light which contains not only the short wavelengths which split off the electrons from the atom, but long waves, too. The photocurrent is not constant in time which shows that a secondary current of considerable greatness is flowing. I have to suppose the rise of a very great space charge in the dyestuff plate which lessens the further photocurrent. The existence of this space charge in the dyestuff plate is proved by switching off light and outer electromotive force. When switching off light and electromotive force I get a very abruptly decreasing current of opposite direction. This current is the ceasing of space charge. The absolute value of space charge is increasing with the increase of outer voltage according to experimental results. The difference of beginning and constant values of photocurrent is proportional to space charge, as primary current is decreased by space charge. The decrease is not constant in time because an equilibrium is developing between the beginning space charge and the intensity of photocurrent. Therefore the photocurrent reaches a constant value in a comparatively short time. We receive a photocurrent of greater percentage in equilibrium under every outer voltage, than before equilibrium. This shows that the equilibrium is more advantageous for the splitting of electrons than the unstable state. The photocurrent and also the dark current are increasing proportionally to the increase of outer voltage, but the percentage decreases. This means that the circumstances are more advantageous for the photocurrent — in connection with dark current — when using of small voltage.

Taking into consideration the results of 8., 9., and 10. experiments we may conclude that the inner photoelectric effect is hindered by colloid water just as it had been found for outer photoelectric effect. On investigation of outer photoelectric effect the loss of colloid and capillary water occurs in vacuum in every case. When measuring the inner photoelectric effect we have to heat the phosphor plate in every case to get measurable photocurrent. As the phosphor regains its colloid water, the photocurrent decreases. (8). (Tables II., III. and IV.).

The photocurrent is increasing with the increase of concentration (Table V.) under every voltage but the percentage, comparing the photocurrent with the dark current, decreases. This may be explained in the following way. The conductivity of phosphor is

Table V.

		Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage	Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage	Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage	Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage	Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage	Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage	Dark current. Unit 10^{-13} Amp	Photocurrent	Percentage
Outer voltage Unit: Volt		10			50			100			150			200			250			300		
—1·0	log conc. gr dyestuff/cm³ dry gelatine	6	6	100	19	16·5	87	35	30	86	51	43	84	67	56	83	83	70	83	99	83	84
—2·0		not measurable	5	—	7·5	14	187	18	25	139	28·5	36	126	39	47	120	49	59	120	60	70	116
—3·0		2	3·5	175	8	12	150	15	21	140	22	31	140	29	40	138	36	50	139	42	59	138
Pure gelatine		1·5	3·5	230	5	8·5	170	10	16	160	15	24	160	20	31	155	25	30	120	30	37	123

increasing more rapidly with the increase of concentration than the photocurrent. Presumably the splitting of electrons is increasing with the increase of concentration (just as it has been found in the case of outer photoelectric effect), but the secondary currents are greater compared with the primary current in cases of smaller concentration than in cases of greater concentration. It may also be explained by supposing smaller secondary currents in plates of greater conductivity (greater concentration).

Summary.

I have measured the inner photoelectric effect of rigid gelatineous dyestuffs. The results are:

1. The photocurrent decreases and reaches a constant value in time. The decrease is proportional with outer voltage in absolute value. The percentage is also decreasing. The absolute value of photocurrent is increasing when outer voltage is increased, but its percentage, calculated according to dark current, is diminishing.

2. The photocurrent is increasing protortionally to outer voltage. The greater the loss of colloid water of phosphor, the greater the photocurrent at every outer voltage. There is not to be found a photocurrent on plates exposed to humidity of room.

3. When increasing the concentration of dye, the absolute value of photocurrent is increasing under every outer voltage but its percentage, calculated according to dark current, is diminishing.

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Über die antibakterielle Substanz des Rettichsamens.

Von St. Koczka und G. Iványovics.

(Eingegangen am 2. März. 1949.)

In einer vorläufigen Mitteilung (1) wurde über die antibakterielle Wirkung eines aus dem wässrigen Auszug von Rettichsamen gewonnenen Öles berichtet. Kurz darauffolgend wurde in einer zweiten Mitteilung die Isolierung, chemische Analyse und biologische Wirksamkeit dieser von uns „Raphanin" genannten Substanz ausführlich beschrieben (2). Man konnte feststellen (3), dass das Raphanin durch Thiolverbindungen inaktiviert werden kann. Unlängst berichteten H. Schmid und P. Karrer (4) über die Isolierung eines Senföles mit antibiotischer Wirkung aus Rettichsamen, das sie — nach Aufklärung seiner chemischen Konstitution — „Sulforaphen" nannten.

Es ist auffallend wie nahe die physikalischen und chemischen Eigenschaften der beiden Öle verschiedener Isolierungsart zu einander stehen. Für Sulforaphen geben Schmid und Karrer folgende Daten an: $Kp._{0.015}$ 125—130°; $(\alpha)_D^{14} = -136°$ (Alkohol); C 41.01, 41.42; H 5.14, 5.39; N 8.06, 8.41, 8.09; S 35.48, 35.58%. Raphanin haben wir (2) durch folgende Daten gekennzeichnet: $Kp._{0.06-0.09}$ 135—142.5°; $(\alpha)_D^{20} = -141°$ (Alkohol); C 41.26; H 5.18; N 8.41; S 33.64%. Die durch uns früher angegebene Formel für Raphanin wurde nur als vorläufige Formel betrachtet. Es ist augenscheinlich, dass die niedrigeren Gesamt-S-Werte nicht auf die ungenügende Reinheit unserer Substanz zurückzuführen sind, sondern auf die Anwendung der Pregl-schen Perlenrohrmethode bei ihrer Bestimmung (5). Noch auffallender ist es, dass der bei Sulforaphen von H. Schmid und P. Karrer gefundene antibakterielle und blastokoline Effekt genau derselbe war, den wir früher beim Raphanin schon festgestellt haben.

Zur endgültigen Entscheidung der Identitätsfrage der beiden Öle, haben wir einige Umsetzungsreaktionen, die durch. H. Schmid und P. Karrer bei der Kontitutionsuntersuchung des „Sulforaphens" durchgeführt wurden, auch beim „Raphanin" erprobt und gefunden, dass das letztere bei analogen Eingriffen dieselbe kristallienen Umsetzungsprodukte in derselben Ausbeute liefert, wie „Sulforaphen". Es entstehen durch Einwirkung: von Ammoniak das „Thioureid" (Ausbeute 51%; Smp. 220°; C 37.50, H 6.49%;) von Anilin das „Phenylthioureid" (Ausbeute 74%; Smp. 121°; C 53.81, H 6.19%), von rauchender Salpetersäure Methansulfonsäure, die als Ba-salz isoliert wurde (Ausbeute 80%; C 7.73, H 1.99, Ba 42.17%).

Für die Identität des „Sulforaphens" mit „Raphanin" spricht ausser diesen Daten auch der Umstand, dass letzteres auf das Molgewicht des Sulforaphen bezogen pro Mol ein labiles Schwefelatom enthält (Gef. 0.99, 1.08); dieser titrimetrisch (0.1n $AgNO_3$) bestimmte Wert spricht zugleich für die Einheitlichkeit und analytische Reinheit unseres Praeparates.

Es ist somit festzustellen, dass das durch H. Schmid und P. Karrer beschriebene „Sulforaphen" mit dem schon früher durch den einen von uns in Gemeinschaft mit St. Horváth isoliertem „Raphanin" identisch ist. Wir danken Herrn Prof. V. Bruckner auch an dieser Stelle für seine wertvollen Ratschläge.

Zusammenfassung.

Es wurde auf Grunde chemisch-analytischer, präparatiewer und biologischer Befunde festgestellt, dass die aus Rettichsamen zweierlei Art isolierten antibiotischen Substanzen „Raphanin" und „Sulforaphen" identisch sind.

Szeged, (Ungarn), Febr. 1949.

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Absorption Spectra of Diastereoisomeric Alkanolamine Derivatives.

Preliminary Communication.

By József Kiss and László Láng.

(Received 10. April 1949)

In preceding investigations one of us established, cooperating with Fodor that the acyl derivatives or aryl-proponol-amines of psi-ephedrine configuration undergo acyl-migration, whereas in the case of corresponding ephedrine derivatives, under similar experimental conditions, this reaction does not take place.

Fodor and Kiss (1) therefore came to the conclusion that in the case of ephedrine derivatives the substituted amino resp. methyl-amino group and the secondary alcoholic hydroxyl take up a spacially distant position — independently from the relative position of the other radicals attached to the asymmetric carbon atoms — consequently we must suppose that the corresponding groups of psi-ephedrine derivatives take up a specially near position.

The correctnes of this statement seems to be supported by the fact that some N-benzoyl-nor-psi-ephedrine derivatives gave with thionyl chloride at low temperature on oxazoline derivative whereas

the corresponding norephedrine analogue was not able to undergo, under the given mild conditions, a similar ring closure. As many important compounds can be found among diastereoisomeric amino alcohols, and the literature proved to be incomplete and erroneous concerning the correct interpretation of the steric structure of some of these compounds, it deemed of interest to examine the ultraviolet absorption spectra of some aryl-alkanolamine-derivatives.

Investigators have already dealt occasionally with the ultraviolet absorption spectrum of ephedrine and psi-ephedrine.

Graubner (2) has established that the optically active l-ephedrine and racemic dl-ephedrine deliver an identical ultraviolet absorbption curve with maxima at 317 and 257 mμ wave lengths.

Marchlewski and Skarzinski (3) have studied the ultraviolet absorption curve of ephedrine and psi-ephedrine hydrochlorides. In aqueous solution dl-ephedrine hydrochloride shows 3 absorption bands, its maxima can be found at 2628, 2564 and 2504 Å, l-ephedrine-hydrocloride, as well as d-psi-ephedrine hydrocloride, gave the same absorptiom maxima.

Wolfes (4) referring to other experiments reports the ultraviolet absorption spectrum of a 1 percent aqueous solution of d-nor-psi-ephedrine hydrochloride. According to him the absorption maximum is betweem 250—260 m. Abildgaard and Baggesgaard-Rasmussen (5) investigated the absorption spectrum of 0.02 and 0.002 mole solution of ephedrine and psi-ephedrine hydrochloride establishing that l-ephedrine and different recamie ephedrines deliver an *identical* absorption curve. The maximum of the d-psi-ephedrines is at 2575 Å slightly below the one of l-ephedrine, otherwise they are nearly of the same type.

Fodor and Csokán (6) studying spectroscopically the structure of the nitrones, also examined the ultraviolet absorption spectra of different-alkoxy-phenyl-β-benzylamino-propanol-amiens. Their investigations were strictly confined to the steric modification of one of the diastereoisomeric pairs synthesized from psi-nitrosites and corresponding to the psi-ephedrine configuration. The absorption maxima were found at 230, 236, 228 resp. 239, 286 and 277 mμ.

In connection with their investigations on the interaction of several chromophores in the same molecule, Kiss, Fodor and Lózsa (7) examined the ultraviolet absorption spectra of some acylated propanolamines. In their study they only discuss acylamines of psi-ephedrin series.

The cited literary data seem to evidence that diastereoisomer alkanolamine pairs were not submitted to systematic and comparative spectroscopic examinations. As in the course of the above mentioned acylmigration experiments a well defined significant difference was found between the derivatives of ephedrine and psi-ephedrine and as this difference could of course only be established among the acylized derivatives, the suggestion was put forward as to whether one can observe a systematic difference in their ultraviolet absorption spectra, as well as in that of the substituted alkanolamines and their derivatives. For this purpose the following diastereoisomeric alkanolamine pairs were submitted to a very thorough examination.

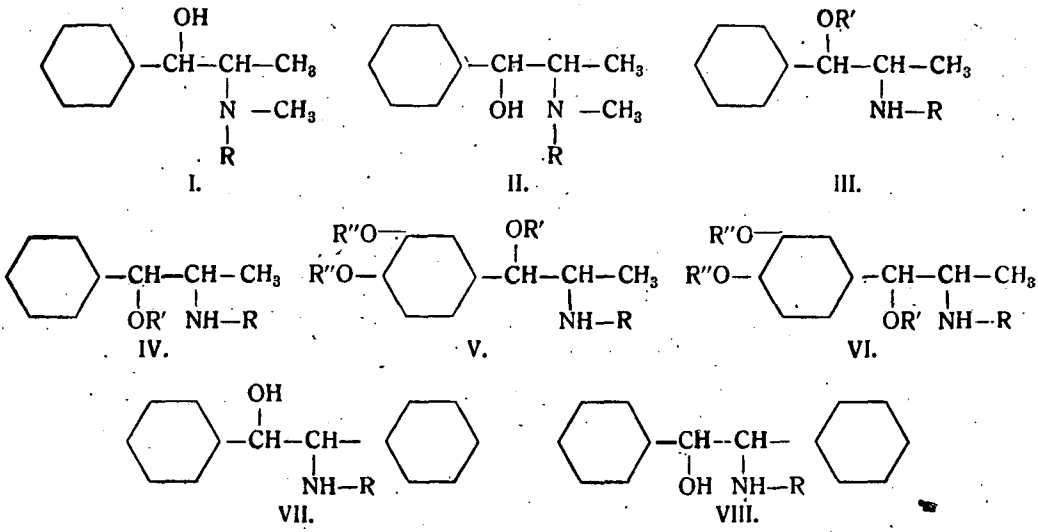
The alkanolamines of ephedrine configuration, needed for our investigations were obtained by catalytic reduction of the oximino-ketones, whereas the diastereoisomers corresponding to the steric structure configuration of psi-ephedrine were prepared by synthesizing them from psi-nitrosites, further by isomerisation of the the resp. ephedrine derivatives with hydrochloric acid. The diastereoisomeric pairs obtained in this manner was a form separated by means of acyl migration.

The experimental results are summarized in the following table:

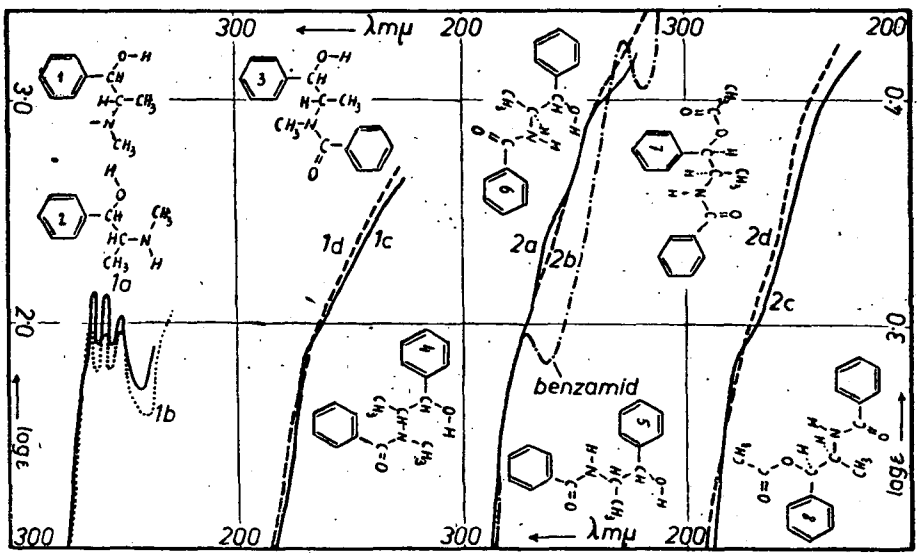
No.	Name of compound	Formula-type	Absorptions maxima in mμ	Log e	Curve
1.	dl-Ephedrine	I. R = H	251, 258, 263	2.03, 2.13, 2.14	I. a.
2.	dl-psi-Ephedrine	II. R = H	251, 258, 265	1.96	I. b.
3.	N-Benzoyl-dl-ephedrine	I. $R=C_6H_5-CO-$	Ascending branch		I. c.
4.	N-Benzoyl-dl-psi-ephedrine	II. $R=C_6H_5-CO-$	Ascending branch		I. d.
5.	N-Benzoyl-dl-nor-ephedrine	III. $R=C_6H_5-CO-$, $R'=H$	Ascending branch		II. a.
6.	N-Benzozl-dl-nor-psi-ephedrine	IV. $R=C_6H_5-CO-$, $R'=H$	Ascending branch		II. b.
7.	N-Benzozl-O-acetyl-dl-nor-ephedrine	IV. $R=C_6H_5-CO-$, $R'=CH_3-CO-$	Ascending branch		II. c.
8.	N-Benzoyl-O-acetyl-dl-nor-psi-ephedrine	IV. $R=C_6H_5-CO-$, $R'=CH_3-CO-$	Ascending branch		II. d.
9.	N-acetyl-3 : 4-di-ethoxy-dl-nor-ephedrine	V. $R=CH_3-CO-$, $R'=H$; $R''=C_2H_5-$	280, 230	3.58, 4.09	III. a.
10.	N-acetyl-3 : 4-di-ethoxy-dl-nor-psi-ephedrine	VI. $R=CH_3-CO-$, $R'=H$; $R''=C_2H_5-$	280, 230	3.57, 4.09	III. b.
11.	N,O-diacetyl-3 : 4-diethoxy-dl-nor-ephedrine	V. $R,R'=CH_3-CO-$, $R''=C_2H_5-$	280, 234	3.59, 4.07	III. c.
12.	N,O-diacetyl-3 : 4-diethoxy-dl-nor-psi-ephedrine	VI. $R,R'=CH_3-CO-$, $R''=C_2H_5-$	280, 233	4.49, 3.98	III. d.
13.	N-acetyl-diphenyl-ethanolamine	VII. $R=CH_3-CO-$	251, 258, 265	2.47, 2.51, 2.59	IV. a.
14.	N-acetyl-diphenyl-psi-ethanolamine	VIII. $R=CH_3-CO-$	252, 258, 265	2.56, 2.66, 2.68	IV. b.
15.	N-benzoyl-diphenyl-ethanolamine	VII. $R=C_6H_5-CO-$	Ascending branch		IV. c.
16.	N-benzoyl-diphenyl-psi-ethanolamine	VIII. $R=C_6H_5-CO-$	Ascending branch		IV. d.

The interpretation of the Absorption Curves.

The light absorption of compounds number 1 and 2 is determined by the phenyl radical capable of causing a mesomeric effect. The saturated side-chain is unable to give a mesomeric effect and absorption is only appreciable around 200 mμ, thus only increasing the extinction of the compounds in the ascending branch. The curves of the compounds are benzol spectra, influenced by an inductive effect. The feebleness of the inductive effect is proved by the fact that the spectra of the compounds are only slightly shifted to-



wards longer wave lengths — in comparison to the benzene spectrum — and that the extinction has hardly increased. The difference in intensity of the curves of compounds number 1—2 indicates that the diastereoisomerism is demostrated by the curves. In

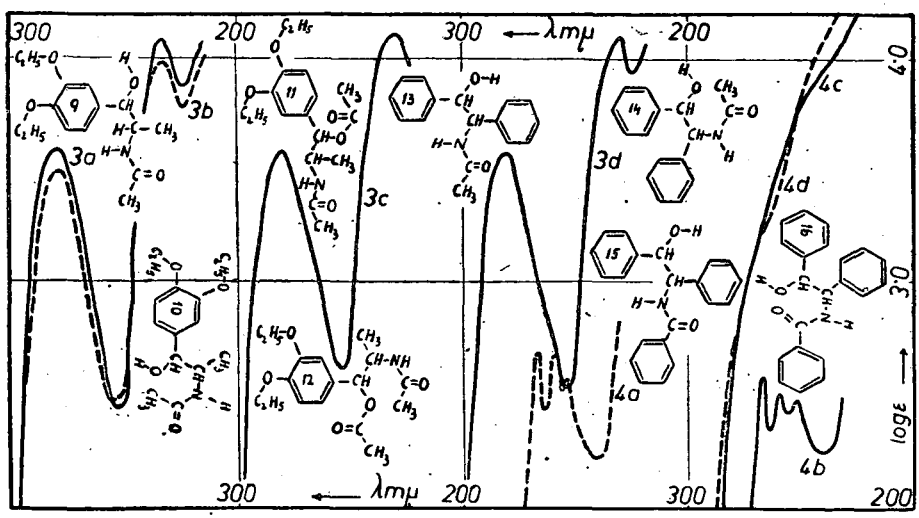


the case of compounds number 13—14 the 2 phenyl radicals being separated by the non-absorbant side-chain possess independent mesomeric systems. The extinction of the compounds is determined by the phenyl radicals A and B.

The side-chain is also idependent with its chromofore carbonamide- imino-hydrine tautomerism. Its extinction exerts its influence in the ascending branch. The absorption curves of the compounds running wich log 0.7 units higher than those of compounds number

1—2, are benzene spectra influenced by an inductive effect with is not very comprehensive, as namely if the extinction values of the 2 phenyl radicals would be added, the curve of compounds number 14 like that of number 2 runs higher. The difference caused by diastereoisomerism is also expressed here. The enhanced extinction of the compounds points to the fact that the side-chain does not inhibit the 2 phenyl radicals from assuming their position in the same plane.

The light absorption of compounds number 9—10 is dominated by the extinction of the diethoxy-phenyl radical. The latter and the side-chain have independent mesomeric systems. The mesomeric effect of the 3 oxygen atoms is inhibited by etherification. The course of the curves of the compounds are almost similar to those of the corresponding dimethoxy-derivatives photographed by Lózsa (7), showing that the mesomeric effect of the oxygen atoms is equally influenced by the methyl, resp. ethyl radicals. The extinctin of the side-chain exerts its influence in the ascending branch. In the light absorption of the diastereoisomers, probably owing to the extinction, there is already no significant difference.



In the case of compounds number 11 and 12 the diethoxy-phenyl radical and the side-chains are independent chromophores. The absorption curve of the 2 compounds is also determined by the axtinction of the diethoxy-phenyl radical. The effect of the side-chains only influences the ascending branch. Thus the curves of the compounds are very similar to those of compounds number 9 and 12. The sharply defined bands of the absorption curves of the 4 compounds indicate that the chromophore radicals do not distrub one anothers extinction.

In the case of compounds 5 and 6, A and B phenyl radicals, owing to the isolating effect of the radicals connecting them, constitute an independent chromophore system. The mesomeric effect of radical A is identical with the phenyl radical of compound number 1 and that of radical B with the one of benzamide.

The light absorption of the compounds is dominated by the extinction radical B. Beside this the absorption of radical A, owing to its feeble extinction, cannot exert any influence. Therefore, the curves of the compounds ought to resemble that of benzamide and truly the position of the curves is identical with that of benzamide. The difference lies in the faintness of the benzamide bands. This cannot even be explained satisfactorily by the fact of the 2 phenyl radicals, owing to steric reasons, not beeng able to take up a position in the same plane. The structureless curve renders the investigation of the diastereoisomeric effect more difficult.

In the case of compounds number 3 and 4, resp. 7 and 8 the conditions are essentially identical, so that their detailed treatment is superfluous.

In the case of compounds number 15 and 16 all — A, B, C — benzene rings have, owing to the isolating effect of their connecting radicals, independent mesomeric systems. Rings A and B may be in the same plane, ring C, however, deviates from this plane. The light absorption of these compounds is also dominated by the extinction of ring B, beside which that of rings A and C can hardly exert any influence. Thus the curves of these compounds are also benzamide curves with an only faintly distinguishable structure. If owing to steric reasons all of the 3 benzene rings would occupy a different plane, this would not influence the course of the curves esentially, in consequence of the feeble extinction of radicals A and B.

Compounds 3—8, furthermore 15—16 are structures with faint bands. If steric models would confirm that already in the case of compounds 3—8, owing to steric reasons, ring A and B enter different planes we could interprete this in the following manner:

If ring B takes up a vertical position in the plane against the light it gives the band structured spectrum of benzamide with a maximally intense absorption. If ring A takes up a vertical position against light, it absorbs with maximal intensity, whereas ring B taking up an angle position, absorbs less intensively and with a shift towards the short wave lengths. The additivity of the extinction of radical B in 2 situations can extinguish the band structure of the benzamide spectrum. To decide the correctness of the explanation one would have to photograph the absorption curve of such a benzamide derivative, in which one of the hydrogen atoms of one of the NH_2-radicals is substituted by an alkyl radical.

Our investigations give evidence of a significant difference betveen ultraviolet absorption spectra of the diastereoisomeric alkalonamines and that of their derivatives. Further examinations are in progress involving similar investigations of still more of such types of diastereoisomeric pairs and careful studies of the ultraviolet absorption spectra of other types of diastereoisomers.

Acknoledgement. The authors are indebted to Gábor Fodor associate professor for having directed their attention towards the diastereoisomeric problems and to professor Árpád Kiss for the interpretation of the absorption curves.

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Zur Lichtabsorption der Komplexe von Aminobenzolsulfosäuren.

Von Á. Kiss und J. Faredin.

(Eingegangen im Januar 1949).

1. *Einleitung.*

Den Komplexen von Aminobenzolsulfosäuren schreibt Pfeiffer (1) eine betainartige Struktur zu (Vgl. Abb. 2, Form. a und Abb. 5, Form. c) U. E. wird diese Behauptung bei den Komplexen von Metanil- und Sulfanilsäure aus sterischen Gründen zutreffen. Die Metalle mit unaufgefüllten äusseren Elektronenschalen werden aber mit Orthanilsäure innerkomplexe Salze bilden. (Abb. 2, Form. b). Um dies zu beantworten wurden die Extinktionskurven der Komplexe von Orthanil- und Sulfanilsäure im Wasser bei Zimmertemperatur ausgemessen (2).

Bezüglich der experimentellen Einrichtung und der Messmethode verweisen wir auf früheren Arbeiten (3). Die Komplexe wurden nach Literaturangaben (4) hergestellt. Da auch die neuen Verbindungen ähnlicher Weise leicht zu erhalten sind, sehen wir von der Wiedergabe der Darstellungsvorschriften ab. Die Reinheit der Komplexe, bzw. die Konzentration der Lösungen wurden analytisch kontrolliert.

2. *Zur Konstitution der Komplexe.*

Bei den Alkali- und Erdalkali-Verbindungen findet eine elektrostatische Bindung zwischen Sulfogruppe und Metallion statt. So dissoziieren diese Komplexe im Wasser elektrolytisch. (1). Bei den komplexbildenden Metallen, mit unaufgefüllten äusseren Elektronenschalen, von der o-, bzw. p-Stellung der Amino- und Sulfogruppen abhängend u. E. entstehen innerkomplexe Salze (Abb. 2, Form. b, bzw. Abb. 5, Form. c). Demgegenüber schreibt Pfeiffer (1) beiden Verbindungsreihen betainartige Struktur zu. Bei den Komplexen der Orthanilsäure findet eine semipolare Bindung zwischen dem

Metallion und Stickstoffatom der Aminogruppe statt. Bei den Orthanilsäure-Komplexen der zweiwertigen Metallen sind die Liganden planar angeordnet, denzufolge können zwei Wassermoleküle in trans Stellung festgehalten werden. Die Sulfanilsäure-Komplexe der zwei- und dreiwertigen Metalle sind koordinativ ungesättigt und können daher ihre freien Koordinationsstellen mit Wassermolekülen auffüllen. Auch die Sauerstoffatome der Sulfogruppe können mit ihren einsamen Elektronen Wassermoleküle binden.

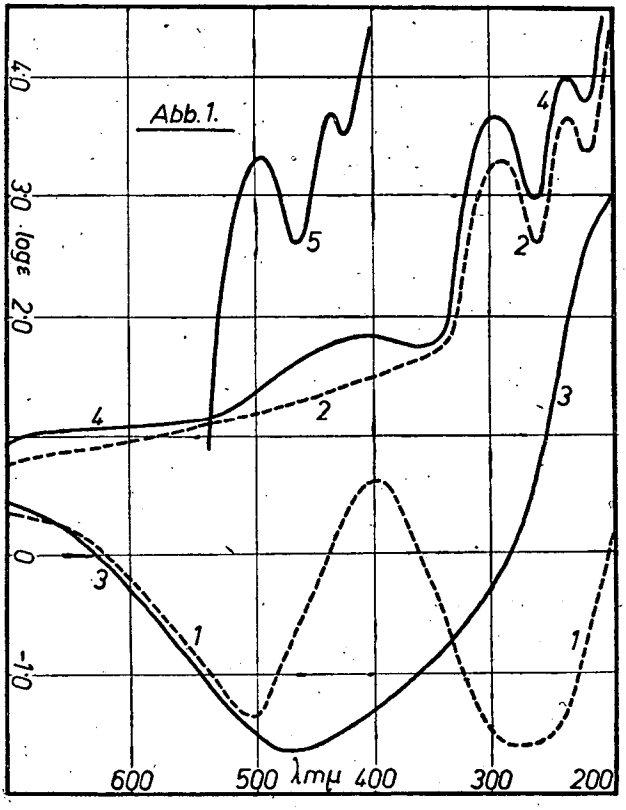

Abb. 1. Kurve 1: $Ni(ClO_4)_2$. K. 2: Co-orthanilat. K. 3: $Fe(ClO_4)_3$. K. 4: Cu-orthanilat. K. 5: Orthanilsäure.

3: *Zum Mechanismus der Lichtabsorption.*

Die Aminobensolsulfosäuren haben sowohl im Grund- als in dem Anregungszustand mehrere, miteinander in Resonanz stehende Grenzstrukturen (5). Der Benzolring und die Aminogruppe bedingen die Mesomerie. Die Sulfogruppe beteiligt sich in der Mesomerie in keiner merkbarer Weise (5).

Wegen der semipolaren Bindung zwischen Stickstoffatom und Metallionen werden in den Komplexen die Grenzformen b (Abb. 2) und c (Abb. 5) vorherrschen. Das Beibehalten der selektiven Absorption der Liganden in ihren Komplexen spricht für die Mesomeriefähigkeit der Aminogruppe.

Der beinahe gleiche Verlauf der Extinktionskurven von Orthanilsäure (Abb. 1, K. 5) und Sulfanilsäure (Abb. 4, K. 1) und ihrer Alkali- und Erdalkali-Komplexe (Abb. 3, K. 1—3, bzw. Abb. 4, K. 2—4) weist darauf hin, dass ihre Extinktionskurven additiver Art aus der selektiven Absorption ihrer Ausgangsstoffe zusammengesetzt sind. Dies spricht für die Dissoziation ihrer Komplexe im Wasser.

In der Lichtabsorption der Komplexe mit koordinativer Bindung beteiligen sich die Liganden, die eigenen Elektronen des Zentralions und die koordinativen Bindungselektronen (6).

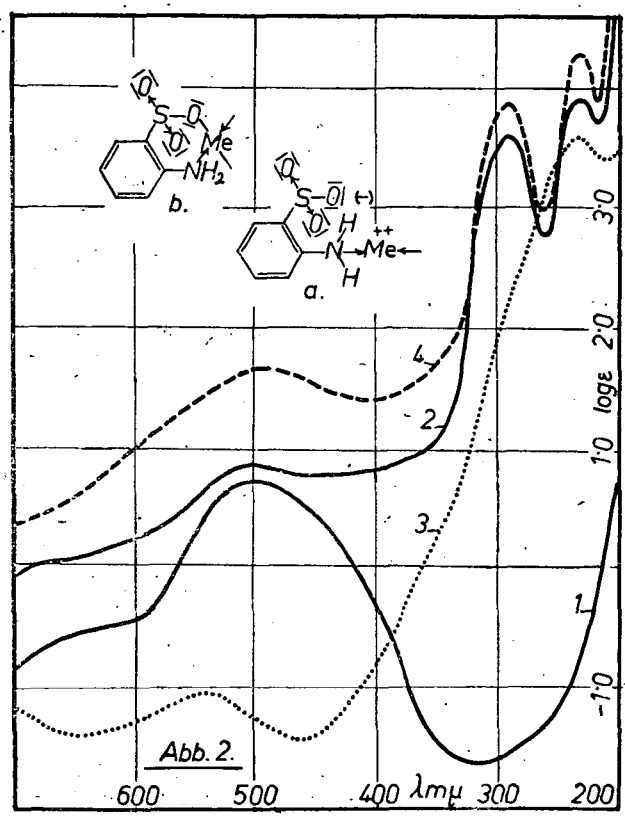

Abb. 2. Kurve 1: $Co(ClO_4)_2$. K. 2: Co-orthanilat. K. 3: $Fe(ClO_4)_3$. K. 4: Fe-orthanilat. a: Betainartige Struktur des Orthanilsäure-Komplexes. b: Innerkomplexe Struktur des Orthanilsäure-Komplexes.

Da in ihren Komplexen die Lage der Banden von Orthanil- und Sulfanilsäure beibehalten wird, (Vgl. Abb. 1—5), ändert die Komplexbildung kaum deren Elektronenanordnung. Nur die Übergangswahrscheinlichkeit wird geändert, worauf die Extinktionszunahme hinweist. Die Extinktion von Orthanil- und Sulfanilsäure wird von den eizelnen Metallionen ganz spezifisch geändert.

Ein Vergleich der Kurven der Orthanil- und Sulfanilsäure-Komplexe, sowie der Perchloraten der entsprechenden Metallionen (Abb. 1, K. 1 und 3, Abb. 2, K. 1 und 3) zeigt folgendes:

Bei den Orthanilsäure-Komplexen der gefärbten Ionen: Cu, Co, Ni und Fe wird die Bandenstruktur des Metallions beinahe voll-

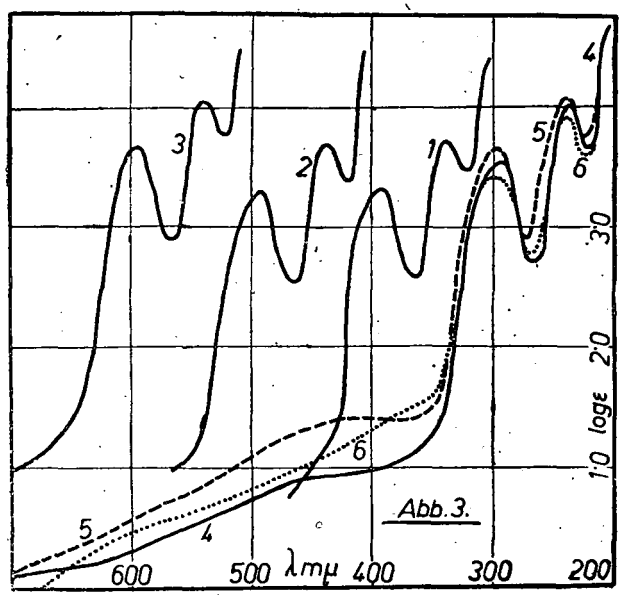

Abb. 3. Kurve 1: Na-orthanilat. K. 2: K-orthanilat. K. 3: Ba-orthanilat. K. 4: Mg-orthanilat. K. 5: Cd-orthanilat. K. 6: Zn-orthanilat.

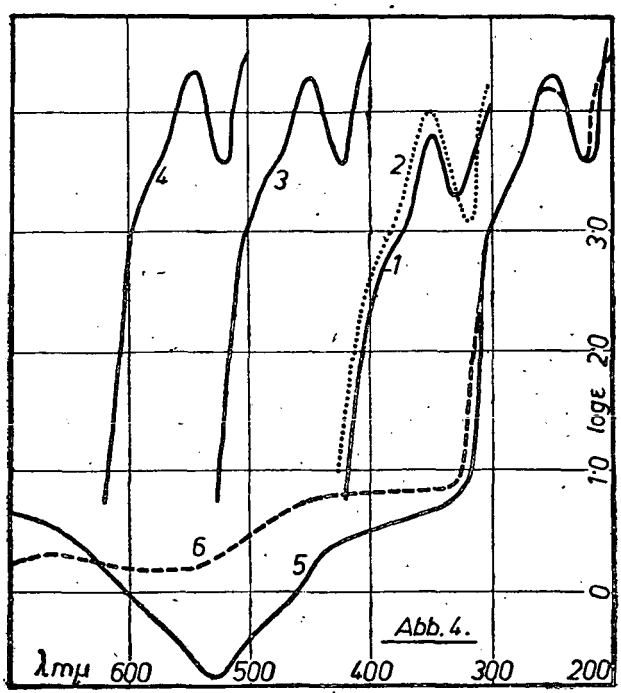

Abb. 4. Kurve 1: Sulfanilsäure. K. 2: K- und Na-sulfanilat. K. 3: Mg-sulfanilat. K. 4: Ba-sulfanilat. K. 5: Cu-sulfanilat K. 6: Ni-sulfanilat.

ständig verwischt (Abb. 1, K. 2 und 4, Abb. 2, K. 2 und 4). Dabei nimmt die Extinktion im Sichtbaren und an der Grenze desselben stark zu. Bei den betainartigen Komplexen von Sulfanilsäure mit den erwehnten Metallionen, wird die Bandenstruktur der Zentralionen schwächer verwischt (Abb. 4, K. 5 und 6, Abb. 5, K. 4)) Somit übt die freie Ladung bei den betainartigen Komplexen eine schwächere Wirkung auf die selektive Absorption des Zentralions aus. als die Ringbildung bei den innerkomplexen Verbindungen von Orthanilsäure. Dies kann durch die starke (durch die, in die wahre koordinative Bindung übergehende) Bindung der innerkomplexen Verbindungen bzw, durch die Ringbildung verursachte

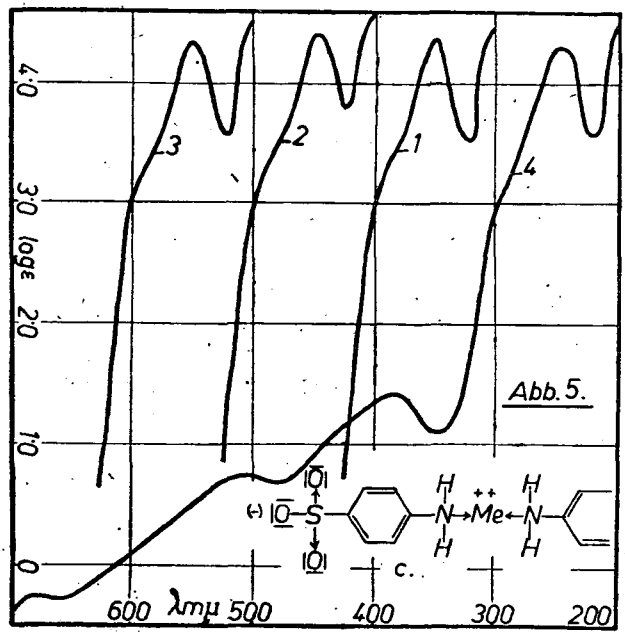

Abb. 5. Kurve 1: Cd-sulfanilat. K. 2: Pb-sulfanilat. K. 3: Zn-sulfanilat. K. 4: Co-sulfanilat c: Betainartige Struktur des Sulfanilsäure-Komplexes.

Deformation des Zentralions und der Liganden verursacht werden (7).

Im Sichtbaren zeigen die Orthanilsäure-Komplexe der ungefärbten Ionen: Mg, Zn und Cd eine schwache Extinktion (Abb. 3, K. 4—6). Dies ist ein Zeichen der inneren Komplexbildung. Bei den entsprechenden Komplexen von Sulfanilsäure (Abb. 5, K. 1 und 3) fehlt diese Extinktion vollständig.

Laut Extinktionsmessungen haben Sulfanilsäure-Komplexe, der Behauptung von Pfeiffer (1) entsprechend, eine betaiartige Struktur. Orthanilsäure bildet dagegen mit den komplexbilden Metallionen, nicht wie Pfeiffer angenommen hat betainartige Komplexe, sondern innerkomplexe Verbindunen.

Zusammenfassung.

Die Extinktionskurven von Orthanil- und Sulfanilsäure und ihrer Komplexe wurden mit den ein-, zwei und dreiwertigen Metallionen ausgemessen.

Die Alkalimetallkomplexe beider Säuren dissozieren in ihren wässerigen Lösungen.

Mg, Zn, Cd, Cu, Co, Ni und Fe bildet, der Behauptung von Pfeiffer entsprechend mit Sulfanilsäure betainartige Komplexe, mit Orthanilsäure dagegen innerkomplexe Salze.

In den Komplexen beider Sären bleibt die selektive Absorption von Orthanil-, bzw. Sulfanilsäure beibehalten, aber ihre Extinktion wird von den gefärbten Metallionen spezifisch geändert.

Als ein Zeichen der wahren Komplexbildung haben Orthanilsäure-Komplexe der farblosen Metallionen: Mg, Zn, Cd an der Grenze des sichtbaren Gebietes eine schwache Extinktion. Demgegenüber sind die entsprechenden Sulfanilsäure-Komplexe in diesem Gebiet durchlässig.

Szeged (Ungarn) Dezember 1848.

Schrifttum.

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2. *J. Faredin:* Dissertation Szeged 1944.

3. *Á. Kiss und M. Gerendás:* Acta chem. mineral. physica Univ. Szeged. 4 (1934—35) 124, 172. 5 (1936—37) 153.

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5. *Á. Kiss und E. Csetneky:* Acta chem. physica Univ. Szeged. 2 (1948) 30.

6. *Á. Kiss und Mitarbeiter:* J. prakt. Chem. (2) 160 (1942) 1. Z. anorg. allg. Chem. 249 (1942) 340, 252 (1943) 172.

7. *Á. Kiss, P. Csokán und G. Nyiri:* Z. physik. Chem. A. 190 (1942) 65.

Abstracts of Lectures Delivered at the Meetings of the Chemical Division of Hungarian Engineers Free Trade Union, Szeged. (8. V. 1948 — 1. II. 1949).

Résumé des Lectures de la Division Chimique de L'Union des Ingénieurs Hongrois à Szeged (8. V. 1949 — 1. II. 1949).

Sitzungsberichte der Fachorganisation Ungarischer Ingenieure in Szeged. (8. V. 1948—1. II. 1949).

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1. *E. Fenyő: Sciences naturelles et materialisme dialectique.* L'auteur examine les découvertes de la physique moderne et de ses recherches il fait des conclusions philosophiques. De ses conclusions il découle que chaque fait nouveau de physique moderne fait ressortir les verités de le philosophie materialiste dialectique dans le sens elaboré par Marx—Engels—Lenin. Chaque fois que dans le méchanique de quanta, la théore de la relativité, la physique de noyau atomique on a materialisé les notions considerées comme des notions spiritualistes tels' que espace, temps, énergie. Ensuite l'auteur explique l'importance de la façon dialectique de penser pour les recherches dans la physique et sciences naturelles modernes.

2. *G. Fodor: Mutarotation in the sterol series.* Lecturer recorded a new series of compounds, i. e. dextrorotatory dibromides of cholesterol and of their derivatives. These formed under heating from the known laevorotatory stereoisomers. This rearrangement proved to be reversible leading to an equilibrium mixture from which both components could be isolated. Dextrorotatory dibromides are more soluble in organic solvents than their stereoisomers. This property could be used in case of acetyl cholesterol dibromide for a useful preparation of trans-dehydro-androsteron. The steric structure of the stereoisomers was intensively discussed. Cf. G. Fodor, Hung. Acta Chim., *1* fasc. 2., 1—10 pages.

3. *Z. Szabó: Stationary states and the enhancement of the yield.* The reaction of carbon and hydrogen has been investigated between 1100—2600° C. The concentration of methane, as function of the temperature shows a course, which can be composed asymetrically from several fundamental reactions. At the lower temperatures reactions occuring between molecules prevail, at the higher temperatures atomic reactions are predominant.

The numerical valuation of experimental data permits the estimation of the constants of these atomic reactions. The yielded reaction heats and the activation energies agree with the theoretically assumed values.

This investigation points to a possibility having some practical importance. Setting in a stationary state instead of an equilibrium it yields a higher concentration than the equilibrical one. Stationary states can occur also before the equilibrium, but only the stationary state behind the equilibrium raises the concentration of the new compound and contributes to the enhancement of the yield. Such stationary states do not arise under conditions leading usually to equilibrium, but they are consequences either or inlet of an extraordinary energy or of appearance of a new reaction.

4. *S. Reitzer: Organic Fluorine Compounds* (Review).

5. *G. Wilheim: Hydrogen fluoride in organic chemistry (Review.)* Lecturer reported about the function and the recent use of HF in organic chemical processes. He recorded the properties of HF, as well as the advantages and disadvantages of its use in chemical reactions. The catalytic effect of HF, showed to be useful in alkylation, acylation, polymerisation and some specific reactions. In

other cases it is present as an fluorinating agent. The investigation of J. H. Simons and R. E. McArthur reported (1947) the oxidation of aromatic hydrocarbons to phenols, by means of HF as catalyst. This new catalytical agent got a great importance in the organic chemical industry.

6. *L. Vargha: Studies in Furan Chemistry.* On treating p-toluenesulfonyl 2-acetobenzofuranoxime (V.) with methanol and ethanol, respectively, in addition to ammonium p-toluenesulfonate four different substances (A, B, C_1, C_2) were isolated. The same *A* ($C_{10}H_8O_3$) and *B* ($C_8H_6O_2$) were produced both in methyl- and ethylalcoholic mediums, but C_1, obtained from the methanolic reaction product ($C_{12}H_{14}O_4$), was found to be different from that of the ethanolic one (C_2, $C_{13}H_{18}O_4$). The constitution of *A* and *B* has been determined by various methods, which definitely established their identities as being 2-methyl-3-hydroxy-chromone (X) and 2-keto-coumaran (XIV), respectively. A probable explanation is given as to the mechanism of the conversion of V into X and XIV.

The constitution of C_1 and C_2 could not be definitely established. Based on analyses and on the fact, that their oximes (XV) could be transformed into X, they represent possibly 2-methyl-chromanone-3-dimethylacetal and diethylacetal (XVI), respectively.

7. *V. Bruckner: Ring closure of isoquinoline derivatives I.* Pfeiffer et al (J. prakt. Chem. (2) *154,* 157 (1940)) obtained a compound from brazilin for which they assign structure 1-(2-hydroxy-4-methoxyphenyl)-3-methyl-6.7-dimethoxy-isoquinoline I. On attempting synthesis of I. by the method described by Bruckner and Fodor (Ber. *71,* 541 (1938) they obtained a compound which was not identical with the compound obtained from brazilin. Therefore Pfeiffer el al assigned to the synthetic product the structure 1-(2-hydroxy-4-methoxyphenyl)-3-methyl-7.8-dimethoxy-isoquinoline. Consequently, the synthetic product of Pfeiffer et al is I and not II, so that the structure of the product obtained from brazilin is still undetermined. The structure of a series of isoquinolines, synthesized by the lecturer, by Fodor, Krámli and Kovács formulated by them as 6.7-dialkoxy-isoquinolines, -which was not accepted unreservedly by Pfeiffer- has been similarly proved by degradation to metahemipinic acid resp. to hydrastic acid. Cf. Bruckner, Fodor, Kovács and Kiss, J. Amer. Chem. Soc., *70,* 2697 (1948).

8. *G. Fodor: On the Ring Closure of Isoquinoline Derivatives. II.* As a continuation of the lecture recorded above lecturer proved that the compound obtained by Pfeiffer et al from hematoxyline for which they assumed structure 1-(2-hydroxy-3.4-dimethoxyphenyl)-3-methyl-6.7-dimethoxy-isoquinoline (I) has still an unknown structure. (I) was namely synthesized by the lecturer and his cow and found to be not identical with Pfeiffer's product. Degradation of this synthetic product to metahemipinic acid supported structure I, therefore the compound of Pfeiffer from hematoxyline now became uncertain. Pfeiffer described a degradation product of this compound (from hematoxyline) and suggested for it structure 1-carboxy-3-methyl-6.7-dimethoxy isoquinoline (II). Lecturer and his cow. synthesized II and found it to be different from Pfeiffer's product. The correctness of structure II for the synthetic product has been confirmed by degradation to metahemipinic acid. Thus, the compounds of Pfeiffer et al can not be isoquinoline derivatives, their structures remaining still to be settled. Cf. Fodor, Bruckner, Kiss and Kovács, J. Amer. Chem. Soc., *71.* in the press.

9. *Á. Kiss: The interpretation of the absorption spectrum of benzene derivatives on the base of the inductive and mesomeric effects.*

In the first part lecturer treats the inductive and electromeric effect exerted by the substituents on the absorption spectrum of benzene. To elu-

cidate this problem, lecturer explains, on the base of photography taken in the Institute, the structure of the extinction curves of some typical benzene derivatives on the ground of a critical survey of the mesomeric structure. He emphasizes, that this method of interpretation can only be applied if it is possible to describe the electron distribution with mesomeric structures, but in the case of the formation of molecular orbitals this is no more satisfactory. The explanation is only correct if it is in agreement with the physical and chemical properties of the compounds and if the recent quantummechanical researches confirm the conclusions (See: Á. Kiss: Magy. Chem. Lapja 3. 1948, 393).

10. *E. Csetneky: The resonance of the sulphogroup.* The lecture treated the results of the investigations on the resonance capability of the sulphogroup, in the cases of the following compounds: benzene sulphoacids and their derivatives and of some aromatic sulfoncompounds. It reported the results of the measurements of the absorption spectra of these compounds, which are as follows: when the sulpho group is connected with an aromatic compound, it is only resonance-capable, if an other resonance-capable group (e. g. $-H_2N$, $-OH$) is attached to the benzene ring, which draws the sulpho group into the resonance of the benzene ring. (Acta chem. physica Univ. Szeged 2 (1948) 30.)

11. *J. Hyross: On the absorption of nitro compounds.* The absorption spectrum gives an information on the change of energy between the ground and excited states. The substituents influence differently the two states having an inductive effect and π electron system of the molecule, and an influence on the formation of mesomeric structures. The structures of the extinction curves of the aromatic nitro compounds differ from the curves of other derivatives of benzene. Although NO_2 is unsaturated and is therefore a mesomery-capable group, it has only a mesomeric effect in the excited state. The curves have three bands which can be found in every nitrocompound very cleary except the strong effect of the solvent disturbes them. The band at 248 m μ proves the existence of the NO_2 chromophor. The p-derivatives have only two maxima, this fact is due to the effect of the p-position of NO_2. (Acta chem, physica Univ. Szeged 2 (1948) 76).

12. *A. Pál: The history and development of kindling a fire and the evolution in match-manufacturing.* This essay is a historical survey, which begins with the age when the prehistoric man reached a certain level of intellect, when he tried and was able to make fire consciously, from several sources of fire available him from Nature. Later on the long way of evolution, man invented the effective ways of kindling a fire independently of Nature; he learned the tricks how to preserve and keep it alive; he invented the various instruments of making a fire and gradually he arrived to the Swedish safety match used today all over the world.

Due of the most important stations of human culture was the fact that man made use of fire and employed it for his own purposes. From this starting point this study leads us along the long course of development of kindling a fire and match-manufacturing.

13. *G. Varsányi: Berechnung der Extinktionskurven von Kobalt-(2)-chloridlösungen.* (Acta Chem. Phys. Szeged 2 (1949), im Druck.)

14. *L. Csányi: Determination of Chromate-Ion with Arsenite and Diphenylamine as Indicator.*

An accurate and widely applicable method is described for the determination of chromate-ion. Chromate-ion can be reduced by acid arsenite solution. The reaction is catalyzed by manganese-ion. The indication was made

with diphenylamine reversibly and catalyzed by potassium iodide. The acidified arsenious acid solution is very constant in strength.

The following solutions are necessary for this method:

1. Decinormal arsenite.

2. Catalyst solution. A common solution of 0,0210 g. of KJ and 0,0050 g. of $MnSO_4$ in 250 ml of water.

3. Indicator solution.

The procedure is as follows: Acidify the sample of the chromate solution with 5—6 ml cc. sulfuric acid and add distilled water to 50—60 ml. Add to the cooled sample 5 ml of catalyst solution and one drop of indicator solution. Let the arsenious acid run into the chromate solution from a buret just so long till the blue color changes to light green.

15. *L. Kalmár: A science applied without understanding it.* Both Mathematics and Natural Science have their basis in reality; this is what insures the applicability of the former to the latter. Though we see often that scientists apply mathematics without understanding it. For the deepening of the gap between mathematicians and scientists, the philosophical idealism is responsible in the first line, under the influence of which mathematics has been developed in a way as if it would have no connection with reality. In the second line, conservatism of the scientists is responsible too, for they prefer to apply mathematics in the form in which it first has been applied, e. g. mathematical analysis in the form before Cauchy's and Weierstrass's criticism, in which it is not to be understood at all. The only way of elimination of the gap in question is to re-formulate mathematics in a perspicious way, in connection with reality, and to re-formulate science so as to apply in it mathematics re-formulated thus. This is a task of the revolutionary scholars of the Eastern European countries developing towards socialism.

16. *D. Kőszegi: Titrimetrische Bestimmung der Salpeter- und Schwefelsäure nebeneinander.* Nach dem Verfasser wird die volumetrische Bestimmung der Mischung die die beiden Säuren im freiem Zustande enthält, durch Titrieren von zwei Proben durchgeführt. (Die eingewogene Substanzmengen sollen möglichst nicht mehr als 0,2 g Gesammtsäure enthalten). Wenn wir die eine Lösung — nach dem Verjagen der zufällig absorbierten CO_2 — mit carbonatfreiem 0.1 n NaOH titrieren, bekommen wir die Summe der vorhandenen Salpeter- und Schwefelsäuremenge. Von der anderen Einwage wird die Salpetersäure jodometrisch bestimmt, in der Weise, dass wir die eingewogene Säuremischung zu einer von 0,3—0,5 g Baryumcarbonat bereiteten wässerigen Suspension geben. Die Salpetersäure setzt eine äquivalente Menge Baryumnitrat frei, welches mit 0,1 n $K_2Cr_2O_7$ jodometrisch bestimmt werden kann. Der Unterschied der beiden Bestimmungen, gibt die Menge der Schwefelsäure.

17. *E. Vinkler: A new formation of 2, 3, 6, 7-tetramethoxythianthrene.* Lecturer found with *J. Szabó*, that — in order to prepare 3,4-dimethoxy-thiophenole — in presence of a little water zincdust reacts vigorously with veratrolsulfonylchloride By treating the reaction mixture with hydrochloric acid they could isolate near the thiol frequently large, but various amount of 2, 3, 6, 7-tetramethoxythianthrene of *Fries*. Beneath the reaction conditions of *Fries* the sulfonylchloride forms the thiol in a good yield. In order to identify the compound they have prepared the disulfoxyde- and disulfonederivative of 2, 3, 6, 7-tetramethoxythianthrene. (June 10 th 1948).

18. *I. Prettenhoffer: Improvement by machine of limeless soils.* In his lecture the author is dealing with the methods of the improvement of the limeless alkali soil covering about 400.000 cadastral acres of the Lowland. He

is writing about the chemical principals of the improvement and in what soil properties the improvement can be carried out by liming and when by spreading with a lime containing subsoil. Spreading has been carried on by hand for a 150 years. The improvement was not succesful everywhere because till now it has been done in a stereotyped manner and without taking the properties of the soil into consideration. On the grounds of the research work of the institute, after stating the conditions of favourable improvement, the possibility of improvement can be stated beforehand by the help of soilexamination under such conditions the work could be started with greater mechanical strenght. The work has been in progress first with dragline and since 1947. with uptodate scrapers of great performance, with them it is possible daily to improve 8—10 cadastral acres of alkali soil. The result of improvement is permanent and the alkali soil, which bore 6—8 cwt of wheat per cadastral acre before improvement, bears 16—20 cwt after the improvement and on it nearly every useful plant can be grown with success.

19. *Ö. Kovács und I. Kandel: Über die Gerbung mit pflanzlichen Naturstoffen. (Zusammenfassender Bericht).*

20. *I. Sarudi: Dosage de l'acide phosphorique sous forme de phosphormolybdate d'ammonium.* L'auteur dose le phosphore contenu dans des produits complexes sous forme de $(NH_4)_3PO_4 . 12\,MoO_3$ de façon que le precipité molybdénique qui était obtenu par deux précipitations successives, est posé après séchage a 160°. D'aprés les données de ces recherches la valeur trouvée calculée en P_2O_5 est de 3,772%, qui ne différe que de peu de la quantité théorique 3,783%. Il démontre l'exactitude de sa méthode par des dosages effectues sur des solutions de phosphates pures de même que par des dosages sur des apatites et pyromorphites.

21. *É. Salgó: Über die massanalytische Bestimmung von Theobromin und Theophyllin.* (Gemeinsame Arbeit mit D. Kőszegi). Theophyllin und Theobromin lassen sich mit der Hilfe des $K_2Hg(SCN)_4$ quantitative bestimmen. Wenn man diese Verbindungen mit n/10 NaOH-Lösung zu ihren Natriumsalzen umwandelt und mit n/10 $K_2Hg(SCN)_4$-Lösung behandelt, entstehen die Mercurisalze: $(Theophyllin)_2Hg$, bzw. $(Theobromin)_2Hg$, und wird gleichzeitig Rhodan in äquivalenter Menge frei. Nun wird die niederschlaghaltige Lösung durch 20 Minuten vorsichtig erhitzt, filtriert und in dem aliquoten Teil des Filtrats das freigewordene Rhodan mit n/10 $AgNO_3$-Lösung abgeschieden. Der Überschuss de $AgNO_3$ wird in salpetersäurigem Medium, in Gegenwart von Ferrisalz mit n/10 KSCN titriert. Als Vorteil der Methode ist zu erwähnen, dass die genannten Purinbasen sich auch neben dem Coffein abscheiden lassen, da das Coffein mit dem $K_2Hg(SCN)_4$ nicht reagiert.

22. *Z. Csürös: Catalyse sélective.*

23. *Z. Szabó: The Catalytic Effect of Metals of Changing Valency on the Corrosion.* An increasing concentration of cupric ion accelerates the corrosion so that $\log(Cu^{\cdot\cdot})$ is a linear function of time, which points to a first order reaction relating to the cupric concentration. The present halogene ions exert an especially strong accelerating effect. The corrosion increases with increasing H-concentration.

The stirring is without influence on the corrosion velocity, which points to the fact that the process determining the velocity is a reaction which does not occur on the phase surface.

The reaction rate can only be controlled by the process: $2Cu^{\cdot} + 2H^{\cdot} + 1/2O_2 = 2Cu^{\cdot\cdot} + H_2O$. So we obtain an equation for the corrosion, in which $[Cu^{\cdot\cdot}]$ is on the first power, and the influences of $H^{\cdot}$ and $Cl^{\cdot}$ ions can also be taken into account.

The catalyzing effect of the halogene ions are based on the formation of complex ions, by which the Cu · activity is still considerably more lowered, than in the case of oxidation. Thus the equation of the reaction rate, of the corrosion speed will be:

$$-\frac{d[Cu]}{dt} = k_1[Cu^{\cdot\cdot}][H^{\cdot}]^2[O_2]^{1/2} \quad \text{resp.} \quad -\frac{d[Cu]}{dt} = k_2[Cu^{\cdot\cdot}][H^{\cdot}]^2\frac{[Cl']^6}{K_2^2}[O_2]^{1/2}$$

where K_2 is the complex constant.

24. *C. Kell: Modern dewaxing methods.* Recitator gives a short description of the theories and apparatus of the classical dewaxing methods and gives their comparison, with modern processes, known under the names of A. B. T., Barisol, Propan, Dr. *Kell* etc. methods. He renders prominent the Dr. *Kell* and the Propan processes, as of such kind, with which you have the possibility for dewaxing directly residues and the mentions also, that the Dr. *Kell* process can select the naphtenic oil parts, from he paraffinic oils during the dewaxing, without using peculiar apparatus for doing that. He speaks also on the solvents used in the processes and enumerates the advantages and the disadvantages of each process.

25. *L. Kalmár: Dialectical features of Mathematics.* Some mathematician do not feel well unless they can work within exactly defined frames; everything outside their actually accepted frames they feel „vague." Other mathematicians are convinced that exactly defined frames are always too narrow. These views correspond to dogmatical and dialectical philosophy, respectively. Irrational numbers, geometrical construction problems unsolvable by ruler and compass, algebraic equations unsolvable by the four first rules and root extraction, integrals which cannot be expressed by elementary functions, etc., are symptoms of the right of dialectical mathematicians. Set theory has shown that such symptoms are not exceptional as one first supposed, in the contrary, in most cases they form the rule and the entities fitting into the frames are exceptional. Recent results in mathematical logic (of Tarski, Gödel, Church) furnish general theorems showing that exactly prescriben frames are necessarily too narrow to catch the reality, even in mathematical field. This is a strong argument for dialectical philosophy.

26. *A. Lózsa: Zur gegenseitigen Beeinflussung chromophorer Gruppen.*

28. *L. Mészáros: Methoden zur Konservierung von Lebensmitteln.* (Review).

29. *P. Simonffy: Syntheses of Butadien.* (Review).

30. *T. Geréb: Dialectical scientific thought.* True scientific thought was always dialectic and — at least in the sphere of the special branche of the scientist — materialistic. Marx and Engels united dialectics with materialism based on contemptorary natural science. Dialectic trend of thought regards the laws of nature as unilateral relations of the complex connections of nature, for the dialectical scientist law of nature has no absolute validity, divergencies between experience and law are forseen by him and explained by further causal factors. Dialectics, contrary to conditionalism, do not only take into consideration the conditions, the constellation and interaction of conditions but also the reaction of the explored phenomenon on the conditions. Human mind can only comprehend relations arbitrarily deprived of its connections, abstract metaphysical trend of thought is therefore a necessary aspect of thought, but only as a transitory stage of dialectical thought. Truth and error in science are not irreconcilable contradictions, truth has also its relative, temporary, unilateral aspects, error on the other hand is a one-sided exageration of some relative truth. Contradictory scientific statements reflect inner contradictions of reality, emphasising opposite sides of reality. History of science developed in

scientific periodicals reflects this truth far better than the intentionally simplified mode of treatment of textbooks.

31. *I. Kiss: Molecular distillation.* (Review).

32. *R. Balló: Plastics.* (Review).

33. *Á. Kiss: On the effects hindering mesomerism.* The only correct interpretation of the extinction curve of the aromatic compounds can be given by taking the following facts into consideration:

the reciprocal effect of the mesomeric and inductive effects:

the effect hindering or promoting mesomerism, the groups of identical or contrasting character in o-, or p- positions;

the effect hindering mesomerism of the group in m- position;

the steric hindrance;

He elucidates the mentioned affects using spectrophotometrical measurements taken in the Institute. (See details: Á. Kiss and E. Csetneky: Acta chem. physica Univ. Szeged. 2 (1948) 30. 37, 132. Á. Kiss, G. Fodor and A. Lózsa: Acta chem, phys. Univ. Szeged 2 (1948) 25. Á. Kiss and R. Pauntz: Acta chem. physica Univ. 2 (1948) 83.

34. *I. Kovács: Dialectics in modern physics.* The lecturer exerted to elucidate the decisive part of main principles of dialectics in the development of modern physics. So at first he demonstrates that the initiation of the category of changes through jump into physics, fully changed the direction of development of modern physics (quantumtheory); he illustrated with examples the transition of quantitative changes into qualitative changes (periodical system, chemistry). He compares the „eternally unchanged" world of classical physics with the processes of change, development transformation, origination and annihilation of modern physics (radioactivity, transmutation of elements). He explained the main lines of development through contrasts. just as how the each other exclusive contrast became each other suppositional, each other supplementary dialectical contrasts .the double character of light and corpuscular radiation). At least he establishes, that how does the right recognition of the principle of coherence lead to important principal significative statement, wich transformed our physical thinking (the coherence between measuring instrument and system to measure; the relation of Heisenberg).

35. *J. Kiss: The stereochemistry of 4-hydroxy-3-methoxy nor ephedrine.* Two 4-hydroxy-3-methoxy-phenylpropanolamines formed from two different psi-nitrosites on synthesizing in an essentially identical manner, they showed various physical constants. To determine this difference lecturer, Fodor and Szekerke invesligated the connection between the derivatives obtained from both psi-nitrosites; furthermore by the method of isonitroso-kefones the suitable other diastereoisomer was synthesized. Based on the literature data the later synthesis favours in all cases the formation of an ephedrine structure. The compound synthesized in this manner was not identical with any of the previous isomers. They established that by one of the acetylated products, synthesized by route of psi-nitrosite, under acid hydrolysis a change of configuration took place, so that one of the endproducts was not a unitary compound, but a molecular compound of the two diastereoisomeric pairs, showing a constant mp. Therefore the psi-nitrosite synthesis in the cases described above also led to a structure of psi-ephedrine, which was no exception on the general rule established in the course of the institutés work. Cf. Fodor, Kiss and Szekerke, (J. org. Chem. *14* (1949) in the press).

36. *E. Fenyő: Mathematique et marxisme.* Les récents développements des sciences matématiques ont produit des résultats trés importants quanté a leurs conséquences philosophiques. La théorie de logique mathématique bien connue

de Gödel démonstre l'impossibilité de soutenir la thèse de l'objectivisme logique. Ceci en effet démonstre que dans chaque système logique il existe des problémes qui sont impossible a résoudre dans ce système fermé. Cela veut dire que la façon de penser antidialectique plutôt dogmatique amène irrévocablement a l'agnosticisme de telle sorte on doit le considérer comme un système incapable à expliquer l'univers. D'un autre point de vue les mathématiques sont fondérement materialistes puisque d'après un des annoncés de Skolen on peut considérer que plusieurs des conceptions de mathématiques comme par exp. les nombres irrationels ne peuvent être compris autrement que comme des abstractions des faits materialistes. L'auteur a analysé en quoi consiste l'intuitionisme mathématique et il a trouvé que les conséquences philosophiques de cette dernier sont les mêmes que les conclusions de l'Hilberticisme. D'autre part il est clair qu'on peut considérer le systéme intuitioniste de Brouwer comme le pendant mathématique de l'intuitionisme philosophique de Bergson. Comme conclusion: les deux écoles extremistes de philosophic bourgeoise: l'objectivisme rationaliste et le mystique irrationaliste en somme disent le même chose et leur combat n'est qu'une lutte de don Quichotte.

37. *L. Kálmán: The Establishment of the Mechanism of Catalytic Reactions Based on Experimental Data.* The establishment of the reaction mechanism usually occurs by the measurement of the reaction rate and the reaction order, which can be determined from it. In the case of complex processes, however, the rate of the simultaneous and consecutive reactions cannot be measured so that this reaction mechanism cannot be established. In such cases the establisment of the reaction mechanism can be done in the following manner: 1. The establishment of the theoretically presumable reactions and mechanism from the data of the analysis. 2. The exclusion of the unlikely kinetic and thermochemical reactions. 3. The justification of the assumed reaction course calculated by the examination data of volume and percentage obtained from the data of the analysis. The given calculation method involves the simplest mathematical calculations and is based on the gas laws, so that it can be easily and widely employed in cases in which other methods are not efficient.

38. *I. Back: Über die Forschungsprobleme der ungarischen Farbstoffindustrie.* (Zusammenfassender Bericht).

39. *I. Marton: The 2 years of the Hungarian dyestuff manufacture.* Reporter lectured on the circumstances, when the Hungarian dyestuff-manifacture started, on its program and on the 2 years experiences. The first step was the rebuilt of some war-plants, to cover the remarkable dyestuff need appearing after the country's deliberation. The principal problem was the building of pilot-plants. During these 2 years, 26 dyestuff-species were manufactured, which weighed 300 tons amounting to abt. 10,000.000.— Ft. The actual manufacture's capacity covers ab 20% of the home-need; at the same time an export started too. The principal manufacture's lines are: sulfurdyes, chromic wooldyes, Nigrosines, as well as some acid-, direct- and lake-dyes. The preliminary plan for 1949 is to manufacture 350 tons of 34 dyestuff-sorts, amounting to 16,000.000.— Ft. This new-industry is a very important one, especially as regards the development of the Hungarian organic-chemical heavy industry.

40. *A. Lőrinc: Actual problems of the Hungarian dyestuff manifacture.* The 3 principal phases of the aniline-dyestuff manifacture are: 1. research, 2. the manufacturing itself, 3. colouring. The expression „colouring" indicates the chemical and technical operations in the textilefinishing-, leather-, paper- and chemical industry, aiming the permanent colouring of goods, based on scientific methods. The colouring can be a general one, that is the dyeing and local colouring; in this case we speak of printing. Local colouring in the leather-and

chemical-industry is unusual. The dyestuff industry in general, or a dyestuff factory can be prosperous only in case of an intensive cooperation with his own colourist as well as with the manufacturing industry's colourists. The real appearing of the colouring is the textile printing, when the colours are placed harmonious side by side by in a way, that the different colourgroups do not trouble eachother even chemically. The Hungarian dyestuff industry's essential interest is not only to increase the employment's possibilities in our country, but to improve their quality, enabling to compete with the foreign countries, products. That is the point on which the export problem is connected with our dyestuffmanufacturing program.

41. *E. Obermayer: Growing cotton in Hungary.* Lecturer states the cotton to be the most important textile raw material of mankind. As Hungary has a great import of cotton, it seems desirable to secure this requirement at least partly by inland production. Cotton growing on the northern hemisphere is generally limited to the 40th grade of northern latitude. The fact, that Hungary lies between the 46th and 48th grades and consequently the growing season is shortened, the mean temperature too low, the quantity of warmth and sunshine reduced, makes here the cotton cultivation especially difficult. Several unsuccesful experiments in cotton growing have been made in Hungary since 165 years. This failure can easily be understood now as the varieties used were always belonging to late maturing types. As shown by recent experiments performed in the Plant Breeding Institute at Szeged, the Upland varieties of shorter growing period brought up to young plants in warm bed give a very sufficient yield. These varieties if made more early by proper beerding and grown under special agrotechnical circumstances determined by the experiment, institute above mentioned may be grown profitably even by sowing directly on the field. In this way in a normal year in the warmer areas of the country it will be possible to approximate the average yield of the foreign cotton growing lands. Since our cotton-fibre proved suitable for industrial purposes we will start a greater breeding work in spring 1949.

42. *Gy. Bácskai: Oxidation and corrosion.* The lecture explains the development of the oxidfilms on the surface of the metals and their role in the corrosion. It describes the mechanism of oxidation of the metals and alloys, separately in the case of the light respectively heavy metals. It reports on the methods, which renders possible the separation of the oxidfilm from the metalsurface and its examination. It touches briefly on the essence of corrosion, illustrating by experiments, the difference between the corrosion of the metalsurfaces protected and not protected by oxidfilm. Finally it states the corrosion investigations on the artificially produced oxidprotectedfilm.

43. *Z. Szabó: Transurans, Urans and the Periodic Table.* Seaborg and Wahl have recently published an article of the chemical properties of elements 94 and 93, indicating that the transuranic elements are members of a group of atoms similar to the rare earths. Calculations concerning the arrangement of electron shells indicate the starting of a new rare earths group at the elements 91 or 92. Investigation and comparison of the physical (the monotonous changes of the specific weights and of the melting points) and chemical properties (the variation of the ionization potentials and the electrochemical behavior) in relation to the periodic system support the opinion that the new group should be started with Actinium because the physical and chemical properties of the elements (Ac, Th, Pa, U, Np, Pu) fit into the character of the III. column.

44. *P. Benedek: Neuere Ergebnisse der Acetylenchemie.* (Vgl. Magy. Kém. Lapja. 4, (1949), 1, 72.)

45. *F. B. Straub: The role of adenosinetriphosphate in muscle contraction.*

The analysis of actin (a protein taking part in muscle contraction) has revealed the presence of bound Ca and bound adenosinetriphosphate. When salts are added to actin, it changes from a globular protein into a fibrous modification. During this change of form, the adenosinetriphosphate in it changes into adenosinediphosphate. This reaction is not due to an adenosinetriphosphate action. Adenosinetriphosphate has strong positive inotropic action on the isolated frog's heart. It is suggested that the polymerisation of actin is connected with the processes of muscle contraction and the known effected of adenosinetriphosphate in model systems is connected with the changes in actin-bound adenosinetriphosphate.

45. *G. Fodor: A newer method for the separation of diastereoisomeric amino alcohols.* (12. XII. 1948.) In continuation of a work on diastereoisomeric amino alcohols (cf. J. org. Chem. *14,* May 1949.) a newer method for the separation of this type of compounds using acyl migration N → O was investigated. Lecturer gave first a survey of acyl migration reactions and then treated the new method in detail. N-Carbobenzoxy-dl-nor-ephedrine and N-carbobenzoxy-dl-nor-ψ-ephedrine could be isolated by treating their mixture with alcoholic hydrogene chloride. The water insoluble ephedrine derivative was recovered unchanged, whereas the ψ-ephedrine derivative underwent acyl migration yielding O-carbobenzoxy dl-nor-ψ-ephedrine hydrochloride, which is easily soluble in water. Each separated carbobenzoxy derivative was then hydrogenated catalytically, and furnished the corresponding amino alcohol besides toluene and CO_2 (Cf. Fodor and Kiss, Nature, (1949) 287). This behaviour is a consequence of the relative steric positions of acylamido and of the hydroxyl groups. In the ephedrine series, however, the method could not be used for the decision of the configuration. On the contrary, in the series of isocylic amino alcohols, e. g. 2-amino cyclohexanol, occurence, or failure of acyl migration reaction surely proves „cis" or „trans" configuration. At the Institute of Organic Chemistry lecturer and Dr. J. Kiss carried out experiments to decide the still unproved configurations of the diastereoisomeirc 2-amino-cyclohexanols, using their benzoyl and carbobenzoxy derivatives.

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